GENERAL PRINCIPLES
OF
PHYSICAL SCIENCE

NOYES.

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THE

GENERAL PRINCIPLES

OF

PHYSICAL SCIENCE

AN INTRODUCTION TO THE STUDY OF THE
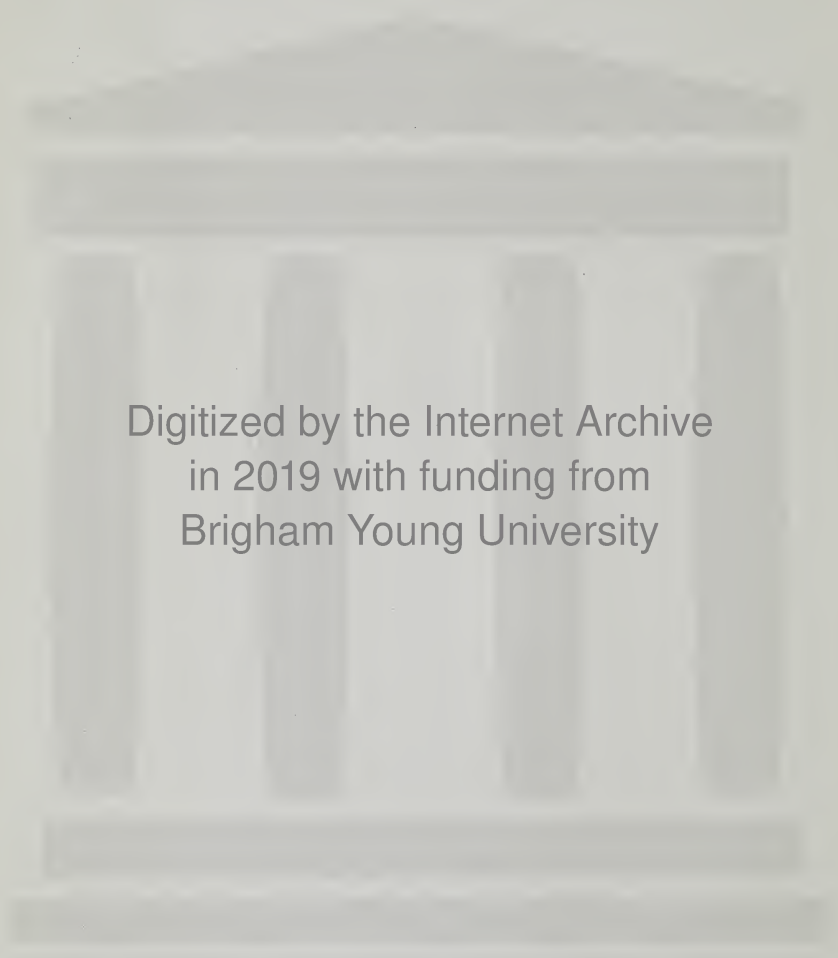GENERAL PRINCIPLES OF CHEMISTRY

BY

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PREFACE.

As the title of this book indicates, its purpose is to present the general concepts and laws of physics and chemistry which lie at the basis of the modern science of theoretical chemistry. It forms the first, introductory part of a projected work upon this science, to be entitled the General Principles of Chemistry, the later parts of which are to treat, in succession, of the General Theories of Chemistry, of the Relations between Physical Properties and Chemical Composition, of the Principles relating to the Occurrence and Equilibrium of Chemical Changes, and of the Principles relating to the Energy-changes Attending Chemical Changes. As the work has had to be discontinued, it has been thought advisable to publish the part already completed, in the hope that it may assist students of theoretical chemistry by supplying, in a concise and consistent form, the essential preliminary knowledge of the fundamental principles of physical science. The method of presentation of these principles may also be of interest to teachers of general physics and chemistry, since an effort has been made to attain precision in the statement of laws and definitions, since the energy-concept has been employed, as far as seemed possible, as the basis of the consideration of other physical concepts, and since the difficult subject of the Second Law of Energetics has been very fully discussed from a non-mathematical standpoint.

The treatment throughout is a systematic, not a historical one. It is essentially non-mathematical, but it is assumed that the reader knows the significance of differential and integral expressions, and that he is acquainted with a few of the simpler operations of the Calculus. On the purely physical side, the treatment is complete and intelligible in itself, in the sense that each term employed is first defined ; but it has been necessary to so condense it, that it can hardly be fully appreciated except by one who has had a fairly

thorough course in general physics : on this side, the book
is intended to serve as a systematic review of the important
physical concepts and principles, and as an aid in acquir-
ing a definite and precise conception of them. It is the
practice of the author to emphasize their significance by
requiring of his classes the solution of numerous prob-
lems. On the other hand, those considerations which
have an especially important chemical bearing are very
fully presented. This is true, for example, of the charac-
teristics of chemical substances, of the concepts of combin-
ing, equivalent, and molecular weights, of the physical
properties and energy-relations of gases, of the work involved
in volume-changes, of Faraday's Law, and of the First and
Second Laws of Energetics. Theories are not discussed at
all in this book; for, in the author's opinion, it is desirable,
in order to avoid producing an exaggerated idea of their
significance, to present fundamental principles independently
of them.

References are not inserted in the body of the book,
but are given in an appendix. Their purpose is to bring
to the attention of the reader more extended discussions
of the subjects treated in the text, to give the authorities
for the numerical data cited, and to indicate the works to
which the author is especially indebted. The notation em-
ployed is summarized in a second appendix ; for much atten-
tion has been devoted to this matter, with the view of
devising for physico-chemical purposes a system consistent in
itself and yet according as nearly as possible with common
usage.

In conclusion, the author wishes to express his great in-
debtedness to many friends for criticisms and suggestions, es-
pecially to Dr. H. M. Goodwin, Prof. H. E. Clifford, Dr. W.
D. Coolidge, Dr. E. Weintraub, Mr. J. G. Coffin, and Mr. M.
Rosenberg.

<div align="right">ARTHUR A. NOYES.</div>

Boston, June, 1902.

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CHAPTER I.

THE OBJECT, THE METHODS, AND THE SUBDIVISIONS OF SCIENCE.

1. **The Object of Science.** — It is the object of science to facilitate the acquirement of a knowledge of the phenomena of nature by devising means for their mental representation, thus replacing by simple operations of thought the slow, laborious process of acquiring that knowledge by the observation of the innumerable isolated phenomena. *It is therefore the object of science to make the completest possible presentation of natural phenomena in such a manner that a knowledge of them can be acquired with the least possible expenditure of effort.*

It is to be noted that the acquirement of this knowledge has two distinct aspects : on the one hand, science aims to make as easy as possible the comprehension on the part of individuals of the knowledge already acquired by mankind ; and, on the other, it aims to add to the total sum of human knowledge by leading to the discovery of previously unknown phenomena.

This statement of the object of science should be carefully noted, in order that the reader may fully appreciate the significance of the various principles and hypotheses employed for the mental representation of phenomena, it being evident that the value of such means of representation is to be estimated solely through a consideration of the extent to which they assist in attaining that object — that is, in facilitating the acquirement of a knowledge of natural phenomena.

It will be clear from this statement that, however abstract or theoretical the methods of science may be, its object, the saving of labor in the acquirement of knowledge, is a concrete and highly practical one. Moreover, the

knowledge which it is the ultimate object of natural science to make readily available, is only the knowledge of actual phenomena, that is, of those natural conditions and changes which lie within the possible range of our experience. Thus, it is not a part of its ultimate object to acquire knowledge in regard to mentally conceived existences, such as the atoms of matter, or the particles of luminiferous ether, which are of such a magnitude and character as to lie far beyond the limits of human perception. By this statement it is not, however, meant to deny that such mental conceptions may be of great scientific value, or that the development of them forms a legitimate part of the process by which the object of science is to be attained; but it is desired to emphasize the idea that such knowledge is the means to an end, and not the end itself.

The value of a knowledge of natural phenomena is so generally recognized that it is not necessary to discuss it. But, in order to guard against a misinterpretation of the statement that the object of science is a practical one, by which was meant that the knowledge aimed at is only that of actual phenomena, it may be added that the value of science arises from the fact that it satisfies the demands of the intellectual faculties of man — his desire to know the phenomena of the external world with which he is in contact — as well as from the fact that it greatly assists in promoting his material welfare.

2. The Methods of Science. — The first stage in the development of a science is the acquirement by observation and experiment of a knowledge of some of the specific phenomena of nature. Some of the isolated facts which it will be the object of the science to correlate, and thus make more readily comprehensible, are first accumulated. These constitute the *data* of the science.

For the correlation of these facts two distinct methods are employed, known respectively as the inductive or empirical method and the deductive or theoretical one.

The inductive method consists in a comparison of the isolated observations with one another, with the object of deriving from them some general statement which shall embrace and sum up a number of the phenomena or of their characteristics. A general statement or principle of this kind so derived is called an *induction,* and the process of reasoning by which it is derived is called *inductive* reasoning; that is, *inductive reasoning is the mental process by which general principles are derived from a consideration of specific cases.* An induction which has been derived by a consideration of a comparatively few specific phenomena, must next be tested as to the extent of its applicability to phenomena in general. If it is found that the principle is one which expresses a common characteristic of a large number of natural phenomèna, and that it is not in contradiction with any phenomenon, it is designated an *empirical law* of nature.

It is important to realize, however, that the universal validity of any such so-called law of nature is always a question of greater or less probability; for, since it is utterly impossible to test the law by applying it to all phenomena, it is never certain that some case will not be discovered in which the law does not hold true. The probability that a law will prove to be applicable to any new phenomenon is of course greater, the greater the number, and the more varied the character, of the phenomena to which it has been already found applicable; and only when these phenomena are extremely numerous and diversified does the probability that the law is universally true approach a certainty.

In the application of an accepted law to a new phenomenon the scientist must therefore always consider the character and extent of the experience which has led to its acceptance : he must not, on the one hand, underestimate, as unscientific minds are apt to do, the probability that a well-established law will hold true in the case of any new phenomenon; nor must he, on the other, dogmatically assert

that the alleged phenomenon is impossible because it is inconsistent with the accepted law. For example, the laws that neither matter nor energy is ever created or destroyed are based on so extensive and varied an experience in all branches of science, that a statement that a process for the creation of matter has been discovered or a perpetual motion machine invented is so improbable as scarcely to deserve scientific consideration. The law that certain substances, the so-called elements, are not transformed into one another by any process whatever, is likewise one to which a very high degree of probability attaches; for the large number of attempts that have been made to effect such a transformation have all resulted in failure. Nevertheless, a consideration of the character of the evidence in favor of the universal validity of this law leads to the conclusion that the probability of discovering an exception to it, although slight, is considerably greater than that of meeting with an exception to the Laws of the Conservation of Matter and Energy; a statement that one of the well-established elements had been transformed into another should, therefore, before it is accepted, be subjected to the closest scientific criticism, and confirmed by conclusive experimental proof.

The discovery that a law is not universally applicable does not entirely destroy, though it does lessen, its scientific value: it only increases the probability that other exceptions to the law will be met with. It is in such a case desirable to establish definitely by experimental investigation the class of phenomena to which the law invariably applies; for, though restricted thereby in scope, the degree of certainty attaching to applications of it is greatly increased.

It is evident that the object of science might be completely attained by the inductive method if it were possible to derive, from an examination of the data, a few principles of such comprehensiveness and definiteness that the vast number of natural phenomena could be represented by

them. Experience has shown, however, that, on account
of the great complexity of phenomena, it is not possible —
at any rate, immediately — to derive inductively universal
principles of this character. Recourse is therefore had to
the second method referred to above: failing to effect
further simplification through a consideration of the facts
themselves and of the laws already derived from them, in-
vestigators attempt to accomplish it by imagining some
state of things which has some of the phenomena, or of
the laws generalizing them, as its necessary consequences.
A concept of this kind, of which no direct experimental
verification has been given, is called a *hypothesis;* that is,
a hypothesis is an assumption of the existence of conditions
of which we have no direct experimental evidence, having
for its purpose the correlation of known phenomena and
the discovery of new ones. A hypothesis of this kind hav-
ing been formed, all its logical consequences are derived
from it, and the conclusions thus reached are tested by
observation and experiment as to their correspondence with
actual phenomena.

The process of reasoning by which such conclusions
are derived is called *deductive* or *a priori* reasoning; that is
to say, *deduction is the mental process by which special con-
clusions are derived from more general propositions.* It is
the inverse of induction. Conclusions which have been
thus derived from hypotheses, but have received no direct
experimental proof, will be designated *theoretical principles*
throughout this work, the term *law* being confined to gen-
eral statements, whether arrived at inductively or deduc-
tively, which have been directly verified by experiment.
The whole body of conclusions derived from a single
hypothesis or a few related hypotheses, constitutes a
theory. The larger the number of otherwise unrelated facts
or empirical laws which the theory serves to correlate, and
the simpler its character, the more valuable and efficient it
is as a means of simplification. Aside from its function as

a means of facilitating the acquirement of existing knowl-
edge, a theory may also be of value by leading to the dis-
covery of new facts and new laws.

It should be distinctly recognized, however, that the
development of hypotheses and theories is *one of the
methods* employed in attaining the object of science, and
not the *object* itself, and that they are to be discarded when
any simpler means of attaining that object is discovered.
It is highly important that the student of science should
constantly keep in mind the radical distinction between
facts and laws on the one hand, and hypotheses and theo-
retical principles on the other; for the history of science
and education proves that there is a great tendency to
attribute to the latter an undue importance, so that a
theory, especially one which has already proved of great
scientific value, may come to be a hindrance to increase of
knowledge and to further progress of the science, by caus-
ing facts inconsistent with the theory, or not comprehended
by it, to be ignored, thus giving to the science a one-sided
development. It is also a very common error to believe
that the knowledge of a group of phenomena or the value
of an empirical law is increased merely by devising a
hypothesis of which the phenomena or law can be shown
to be a necessary consequence. Thus, by reason of the
fact that no definite hypothesis in regard to the nature of
electricity exists, it is apt to be thought that the knowledge
of electrical phenomena is vague and unsatisfactory, which
is by no means the case. If a theory were devised which
brought to light new relationships, not previously recog-
nized, between electrical phenomena it would, indeed, be
of scientific value. If, without doing this, it merely "ex-
plained " a law relating to those phenomena by showing it
to be the consequence of a certain assumption, it might, if
adopted seriously as a part of the science, be an encum-
brance to it, not an aid; for a hypothetical element which
might lead to false conclusions would be introduced, with-
out a compensating advantage. If it be fully appreciated

that the object of science is to make known the phenomena of nature, and not to answer the question why they are so, there will be less danger of attributing an undue weight to hypothetical considerations.

3. **The Subdivisions of Science.** — For the sake of convenience, the vast number of natural phenomena with which science as a whole has to deal are classified into several distinct groups, which can be treated separately to a certain extent. The systematized knowledge relating to these groups of phenomena constitutes the separate sciences. These may be primarily subdivided into three classes : first, the abstract sciences, logic and mathematics, which treat, qualitatively and quantitatively respectively, of the *necessary* relations between phenomena — that is, of the relations which are common to all phenomena, and have been so impressed on the mind by universal experience that they have become conditions of thought ; second, the abstract-concrete or physical sciences, chemistry and physics, which treat of the properties of substances and bodies in the abstract — that is, without reference to any definite aggregates ; and third, the concrete sciences, which treat of the properties of definite aggregates, for example, astronomy, geology, biology, and anthropology, which treat of the heavenly bodies, the earth, living bodies, and man, respectively.

The provinces of the two physical sciences, chemistry and physics, may be defined as follows. *Chemistry* treats of the specific properties of chemical substances, both in the pure state and as components of mixtures, and of their transformations into one another. *Physics* treats of the properties of bodies without reference to the chemical substances contained in them, and of all changes except those involving transformations of chemical substances. The terms used in these definitions are explained in sections 6 and 9.

This Part of the book is devoted to the fundamental considerations underlying both of these sciences. It has therefore been entitled The General Principles of Physical Science.

CHAPTER II.

4. The Fundamental Concepts.—The study of natural phenomena has led to the adoption of four most fundamental concepts, or abstract ideas, called *space, time, matter,* and *energy.* As some, or all, of these concepts are involved in the explanation of every phenomenon, their characteristics, the laws relating to them, and the units employed for their measurement will be first considered.

5. Space and Time.—The concepts of space and time have become familiar to us from continual experience. They are so fundamental and abstract in character that any definition of them would be only a substitution of terms scarcely more intelligible than the names themselves.

The change of the position of a body with reference to some point in space is called *motion.* The rate at which a moving body changes its relative position, or the ratio of the distance (l) traversed to the time (τ) is called its *velocity* (u). If the motion is not uniform, the ratio of very small intervals of space and time must be taken; that is, $u = dl : d\tau$. The rate at which a moving body changes its velocity is called its *acceleration* (a); that is, $a = du : d\tau$.

For the measurement of space, time, and other physical quantities, a great variety of units has been employed at different times and places; but in scientific considerations a single system of units, known as the *absolute* or *centimeter-gram-second* (*C. G. S.*) *system,* has now been almost universally adopted as the standard one. Units which are exact decimal multiples of those in this system are, however, also commonly employed. The unit of length in this system is the *centimeter* (*cm.*), which is defined to be one one-

hundredth part of the distance between two scratches on a standard platinum-iridium bar kept at Paris, when the bar is at the temperature of melting ice. For the measurement of surfaces the square centimeter (sqcm.), and for that of volumes the cubic centimeter (ccm.) is employed. Another unit for the measurement of volumes is also in common use, especially in chemical work; this is called the *liter* (*L.*), and is by definition the volume of 1000 grams of water at the temperature of its maximum density: this volume is very nearly equal to 1000 ccm. The unit of time adopted is the *second*, or $\frac{1}{86400}$ part of a mean solar day, which is the average, determined throughout the year, of the intervals of time elapsing between the successive daily transits of the sun over the meridian at any place on the earth's surface.

6. The Concepts of Matter and Energy. — Experience shows that different portions of the space about us, and the same portion of space at different times, affect our senses differently, giving rise to distinct mental impressions, which are known as *phenomena*. The existence of such mental impressions leads to the conclusion that there exist in our surroundings real things of limited extension which give rise to those impressions; these inferred realities are called *objects, bodies,* or *substances,* and the various powers of affecting the senses which they possess are called their *properties*. The choice between the three terms, object, body, and substance, depends on the standpoint from which the properties are considered. The thing giving rise to the impressions is called an *object* when it is desired to denote the properties of a definitely bounded portion of space, the idea of a definite form being implied; a *body* when it is desired to denote the properties of a definite portion of matter; and a *substance* when the properties are considered more abstractly, without reference either to their spacial extension or their association with any definite amount of matter. Thus we speak of the image of an

object in a mirror or of the shadow cast by an *object*, for these are phenomena in which the form of the thing giving rise to the impressions comes prominently into consideration; we speak of the attraction of two *bodies* for one another, or the work done by a moving *body*, or of the laws of falling *bodies*, for these are phenomena independent of form but closely connected with quantity of matter; and, finally, we speak of the solubility or the melting- or boiling-point of a *substance*, for these properties are not affected either by the form or by the quantity of matter considered. Many properties, to be sure, like color or hardness, are common to objects, bodies, and substances, the usage then being determined by the connotation in the directions stated which it is desired to give to the term. The not uncommon use, especially in descriptive chemistry, of the word body to designate a chemical substance, is inappropriate and unnecessary. The properties of substances when so expressed as to be characteristic of them and independent of the quantity of matter or form which bodies composed of them may possess, are called *specific properties;* thus, specific gravity, specific volume, crystalline structure, specific heat, are specific properties of substances, but weight, volume, form, and heat capacity are properties of bodies rather than of substances.

It is found now that there are certain properties, specifically described in the following section, which are possessed by all bodies, and which in a definite body do not undergo a change in magnitude under any circumstances whatever, no matter how great may be the changes in its other properties. These facts have led to the conception of the existence of something that gives rise to the localization of the phenomena from which are inferred the existence and properties of bodies, and to the constancy and persistence of certain of their properties. This conceived entity is called *matter*.

Most of the properties of bodies, however, are found to undergo great changes, some of them entirely disappearing, and other new ones taking their place. This fact leads to the conception that there exists in the universe some thing or things other than matter which, by association with it, gives rise to the changes in properties which bodies exhibit, and gives to them the power of producing changes in the properties of other bodies. The changes produced are very varied in character; thus, they may consist of changes in the relative position, the state of motion, the temperature, the volume, the form, the state of aggregation, the chemical composition, or in almost any other property, of the bodies concerned. The powers to produce such changes, moreover, arise from apparently quite distinct characteristics in the bodies possessing them, such as motion, attraction, difference of pressure or temperature, electrification, and chemical affinity. It is found, however, that such powers often quantitatively replace one another, and often give rise to identical effects. The changes in properties and the power to produce them are therefore conceived to arise, not from a number of distinct entities, but from a single one, which is capable, however, of manifesting itself in a variety of ' different ways. That which gives rise to the changes in the properties of bodies and to the power to produce such changes is called *energy*. This definition is obviously only a qualitative one. It is sufficient, however, to enable the presence of energy to be recognized; thus, whenever any change in the properties or relations of bodies occurs, it shows that an energy-change is taking place, and whenever a body exhibits the power of producing changes in other bodies, it is to be inferred that it possesses energy.

The general principles relating to the concept of matter, and the properties of bodies most closely connected with it, will be discussed in Chapter III; while those relating to energy, and changes in the properties of bodies considered with reference to it, will form the subject of Chapter IV.

CHAPTER III.

7. Matter, its Quantitative Measurement, and the Law of its Conservation. — Experience shows that when a moving body comes in contact with another body and thereby parts with some or all of its motion, changes are produced in the condition and properties of both bodies, for example, in the directions and rates of their motion, in their forms, or in their temperatures. A moving body therefore possesses energy in virtue of its motion : such energy is called *kinetic energy*. Now it is found that the kinetic energy which a definite body moving at any definite velocity possesses is an invariable quantity characteristic of the body, and entirely independent of its other variable properties, such as its volume, form, temperature, or state of aggregation : this property of a body which determines the quantity of kinetic energy it possesses when moving at a definite velocity is called its *capacity for kinetic energy*, or its *mass*. Secondly, experience shows that any body located at a distance from another body tends to approach it, and does in fact move towards it, unless prevented by some other cause. The bodies therefore possess energy in virtue of their relative position and inherent tendency to approach each other : such energy is called *gravitation energy*. Now, it is found that the gravitation energy which a definite body possesses, when placed at any definite distance from any definite second body, is an invariable characteristic of each of the two bodies, and entirely independent of the other variable properties they may exhibit : this property of a body, in virtue of which it possesses under the stated conditions a definite quantity of gravitation energy, may be

called its *capacity for gravitation energy.* This quantity is mathematically defined in Chapter IV.

Thus there are two properties of a body which are persistent, inherent ones, not detachable from the body, and therefore differing markedly from its other variable properties, which are only temporarily associated with it. It is therefore natural to attribute these constant properties to the existence in the body itself of something which gives rise to them, an assumption which simplifies the interpretation of phenomena : that which gives rise to these constant properties is called *matter.*

The *persistence* of these two properties is, however, by no means all that is implied in the concept of matter. A further inference is to be drawn from the fact that every portion of space which is capable of giving rise to *any* mental impression whatever, is always capable of giving rise to those definite impressions from which are inferred the properties which have been called the capacities for kinetic and gravitation energy. This inference is, that matter is that which gives rise to the localization of the complex of properties which certain portions of space exhibit. Even though, on the one hand, it must be admitted that the existence of matter is inferred only from the various energy manifestations which bodies exhibit, it must be acknowledged, on the other, that there are no manifestations of energy except those which are associated with the manifestations of it that have led to the adoption of the concept of matter : in a word, the two assumed entities, matter and energy, are indissolubly connected in our experience. The concept of matter, therefore, would still remain an important one, even if it were admitted, as some scientists have contended, that matter can be fully interpreted in terms of energy ; for it is the expression of certain *permanently* associated relations which are involved in every natural phenomenon.

The two properties which have most directly led to the assumption of the existence of matter are, as has been

just seen, the capacities for kinetic and gravitation energy. These two quantities are, however, in the case of definite bodies strictly proportional to each other; for, according to Newton's Law of Gravitation, the force of attraction between any two bodies (or the degree of their tendency to approach each other) is directly proportional to the product of their *masses,* and inversely proportional to the square of the distance between them; and this force of attraction, though not identical with the invariable property of bodies which has been designated their capacity for gravitation energy, is nevertheless proportional to it in the case of different bodies, provided the force of their attraction be measured with reference to a definite body placed at a definite distance from them.

To distinguish these two properties, the brief terms mass and weight are appropriately employed. These may be defined as follows, some standard body (like the kilogram-prototype at Paris) being first adopted as a unit of mass and weight : The *mass* of any body is the ratio of the kinetic energy it has, to that which the unit-mass has, when both are moving with the same velocity. The *weight* of any body is the ratio of the gravitation energy it has, with respect to the earth, to that which the unit-weight has, when both are located at the same point. Then it follows from Newton's Law that mass and weight are numerically equal, and that either of them may be taken as a measure of *quantity of matter (m).*

Since matter is an abstract concept similarly related both to kinetic and to gravitation energy, and since it possesses other less definite connotations, it is inappropriate that quantity of matter should be designated by either of the concrete terms mass or weight. Moreover, great diversity of usage exists in this respect, since the term mass is commonly employed by physicists on account of the confusion which arises in physical considerations from the use of the term weight to designate both a force and a quantity of matter; while the term weight is generally employed by chemists, since it is a direct expression of

the property actually measured, since it is the term univer-
sally employed in ordinary life and in commercial transac-
tions, and since the identification of quantity of matter with
capacity for kinetic energy, mass, is at least equally inappro-
priate with its identification with capacity for gravitation
energy, or with weight. In order to avoid this impropriety
of using one word to express two distinct ideas, and to do
away with the diversity of usage referred to, it would be
necessary to introduce at least one new term. For example,
it has recently been suggested to use the word *mass* to des-
ignate quantity of matter in the abstract, *kinergity* to signify
capacity for kinetic energy, and *weight* to represent the
force of attraction towards the earth. Though the adoption
of some new third term would be conducive to much greater
clearness in dealing with the fundamental concepts of sci-
ence, it is not advisable to make use of unusual expressions
in an elementary treatise, except in cases where their em-
ployment avoids really serious confusion in the subjects
treated, or avoids frequent and lengthy circumlocutions.
Throughout this work, therefore, the term weight will be
commonly employed, in accordance with the usage of most
leading chemists, to designate quantity of matter.

The unit-quantity of matter employed in scientific work
is called the *gram*, and is defined to be one one-thousandth
part of the quantity of matter in a standard piece of plati-
num-iridium kept at Paris. The mass and weight of the
gram are *approximately* equal to those of a cubic centimeter
of pure water at the temperature of its maximum density.
Recent determinations of the ratio between the weight of
the standard gram and that of this quantity of water have
given as the most probable value 1:0.99996, so that the
difference between the two quantities may almost always be
neglected.

The term *density* (D) is employed to designate the quan-
tity of matter in the unit of volume; that is, $D = m/v$.
The density of a body is obviously almost exactly equal,

when the centimeter-gram-second system of units is employed, to the ratio of the weight of any definite volume of the body to that of an equal volume of water at the temperature of its maximum density. This ratio is called *specific gravity*. The reciprocal of the specific gravity or density of a body, or the volume occupied by one gram of it, is called its *specific volume* ($\underline{v}$); that is, $\underline{v} = v/m$.

When two or more different substances are uniformly distributed throughout the same space, it is customary to employ the term *concentration* (c) to designate the weight of any one of them in the unit of volume.

It has been seen that, however radical may be the changes produced in the other properties of a body, its mass and its weight determined under the same conditions remain unchanged, a fact which is commonly expressed, adopting the concept of matter, by the statement that *matter is not created nor destroyed by any process whatever.* This principle is known as the *Law of the Conservation of Matter.*

This fundamental law has been inductively derived from a very large number of experiments, including many chemical analyses and syntheses. Recent experiments, in which chemical reactions were caused to take place in closed vessels whose weights were determined before and after the change, have shown that the variation in the weight of the reacting bodies certainly does not exceed one one-millionth part. Thus in one experiment, 86.75 grams of silver sulphate and 238.25 grams of water were placed in one arm of a ∩-shaped glass tube and 200 grams of crystallized ferrous sulphate and 125 grams of dilute sulphuric acid in the other arm, and the tube was hermetically sealed and weighed. The tube was then inverted, whereby the two liquids became mixed and a reaction took place, resulting in the production of metallic silver and ferric sulphate. The tube was then weighed again, and was found to have an apparent weight of 0.00013 gram less than that at first, correspond-

ing to a decrease of only $\frac{1}{1800000}$ part of the weight of the reacting ferrous and silver sulphates. As this small apparent decrease may well have been due to error in weighing, no significance is to be attributed to it. But it is to be noted that this experiment only proves that the Law of the Conservation of Matter is not inaccurate in this case by a greater amount than that mentioned. This illustrates, moreover, the general principle that, since all measurements are subject to a greater or less experimental error, it is not possible to prove the absolute exactness of any law. It is, therefore, always important to state within what limits the accuracy of a law has been tested.

8. The States of Aggregation and Other Physical States of Matter. — When to a homogeneous solid substance, like a mass of ice, kept under a definite pressure, for example that of the atmosphere, heat is continuously imparted, the following phenomena are generally observed: The substance first exhibits a steady rise in temperature attended by a slight increase in volume. When a definite temperature has been reached, no further rise of temperature occurs for a time, but the substance ceases to be homogeneous, and becomes resolved into two parts, one of which, in the so-called liquid state, possesses very different characteristics from those of the other unchanged solid part. This definite temperature, which is that at which the solid and liquid states of the substance coexist in equilibrium with each other, is called its *melting-point;* it varies slightly with the pressure to which the substance is subjected. When the solid part has disappeared and the substance has become a homogeneous liquid, a continuous rise of temperature again takes place, attended generally by a small increase in volume, until another definite temperature is reached, at which the substance again loses its homogeneity, going over first partly and then completely into the so-called gaseous state, in which it exhibits an entirely new set of properties. This temperature, which is that at which under

any definite pressure the liquid and gaseous states of the substance coexist in equilibrium with each other, is called its *boiling-point;* it varies greatly with the pressure upon the substance. Finally, after the substance has gone over completely into the gaseous state, its temperature again begins to rise, and it continues to do so indefinitely as long as heat is imparted; this rise of temperature being attended by a relatively large, continuous increase in volume. If, on the other hand, heat is withdrawn from the gas, the substance undergoes the same changes in the reverse order. It should be added, however, that this behavior is exhibited in all its details only by pure chemical substances (§9), and that some of these, when under certain pressures, pass directly from the solid to the gaseous state, and *vice versa,* without assuming an intermediate liquid state.

The passage from the liquid or solid to the gaseous state can always be brought about by decrease of pressure, as well as by increase of temperature. Thus, if at a definite temperature the pressure on a liquid or solid substance is steadily reduced, it retains its state, increasing slightly in volume, until a definite pressure is reached; it then begins to go over into the gaseous state, and the pressure can not be further reduced until the whole substance has become a homogeneous gas. Then the pressure can be diminished and the volume of the substance increased indefinitely without its becoming again heterogeneous. The pressure at which at any definite temperature the liquid or solid state and the gaseous state of the substance coexist in equilibrium with each other is called its *vapor-pressure.* A clear conception of this property is so important that an experiment illustrating it will be here described. A tube closed at one end, 100 cm. in length, is filled with mercury, and is inverted over a deep trough also containing mercury. The mercury column in the tube then stands at a definite height, say 76 cm., above the free surface of the mercury in the trough, its weight being supported by the pressure of the atmosphere

upon that surface. The tube is kept at a constant tempera-
ture, say 20°. At the bottom of the tube a very little liquid
ether is introduced, and this rises into the vacuum above the
mercury, and completely vaporizes. The mercury column
then falls, owing to the pressure of the ether-vapor upon its
upper surface. Small additional quantities of ether are
successively introduced, and the column continues to fall
until such a quantity of ether is present that it no longer
completely vaporizes, but remains in part in the liquid state.
Further additions of ether then have no further influence on
the height of the mercury column, which remains constant
at 33 cm., the difference (43 cm.) from the original height
(76 cm.) representing the vapor-pressure of ether at 20°.
If the tube is now pushed down into the mercury trough, it
becomes more nearly filled with mercury, the space occupied
by the ether-vapor is reduced, and some of it liquefies, but
the height of the top of the mercury column above the free
surface of the mercury remains unchanged at 33 cm., since
the pressure exerted by the ether, its vapor-pressure, remains
unchanged. If finally the tube is pushed down so far that
the length of it above the free mercury surface is less than
33 cm., all the ether liquefies; for the pressure exerted upon
it, which is always that of the atmosphere diminished by
that corresponding to the weight of the column of mercury,
is now greater than the vapor-pressure (43 cm.) of ether at
20°. — The vapor-pressure of a liquid or solid increases
rapidly with rise of temperature; thus, expressed in centi-
meters of mercury, that of ice is 0.19 at — 10°, and 0.46 at
0°, and that of water is 0.46 at 0°, 2.35 at 25°, 9.20 at 50°,
28.9 at 75°, 76.0 at 100°, and 174.4 at 125°. When a liquid
has acquired, through an increase in its temperature a vapor-
pressure which is greater by an indefinitely small amount
than the external pressure to which it is subjected, it will
evidently drive back this pressure and go over into the
gaseous state; in other words, it will boil. The *boiling-point*
of a liquid is therefore that temperature at which its vapor-

pressure is equal to the external pressure under which it stands. Thus, water boils at 100° under the normal atmospheric pressure of 76 cm., for its vapor-pressure is 76 cm. at that temperature; and from the vapor-pressure values just given it is evident that it would boil at 50° if the external pressure were reduced to 9.2 cm., and at 0° if it were reduced to 0.46 cm.

A substance can be made to pass also from the solid to the liquid, or from the liquid to the solid state, by variations of pressure; but if it is not near its melting-point, the changes of pressure required are enormous. Moreover, increase of pressure tends to cause some substances to assume the solid state, and others, the liquid state; the direction of its influence is therefore not uniform.

These three different states into which matter can be brought by varying the temperature or pressure, and in one or more of which every substance exists, are called its *states of aggregation.* This name has been adopted because it is commonly assumed that in the different states the particles composing the substance are differently aggregated to form the mass.

The characteristics of substances in the three states may be next considered. The behavior under diminution of pressure, which has been just described, furnishes the best basis for a definition of the gaseous state of aggregation. That is, a substance is called a *gas* if it increases in volume indefinitely without losing its homogeneity when the pressure upon it is diminished and its temperature is kept constant. Under the usual conditions of pressure and temperature gases differ from liquids and solids also in the following respects: the volumes of gases vary much more with variations of pressure and temperature than do those of liquids or solids; and the densities of the former are very much less than those of the latter. Thus, if the pressure upon a quantity of air at 0° under the pressure of the atmosphere is doubled, its volume is reduced 50 per cent.,

while the same change of pressure causes a decrease in the volume of water at 0° of only 0.005 per cent.; if air at 0° is heated to 100°, keeping the pressure constant, it increases in volume by 37 per cent., while water increases in volume by 4.3 per cent. between the same temperatures. The density of air at 0° under the pressure of the atmosphere is 0.0013, while that of water under the same conditions is 0.9999, or 770 times as great, and that of ice is 0.917, or about 700 times as great. Highly compressed gases, however, do not differ greatly from liquids in these respects; in fact, by suitable variations of temperature and pressure the two states can be made to pass over continuously into each other.

It is found that gases can always be converted into liquids by sufficiently reducing their temperature, but that, when the temperature exceeds a definite value, called the *critical temperature*, which varies with the nature of the gas, they cannot be so converted by increasing the pressure upon them while keeping the temperature constant. Thus, air at the ordinary temperature does not become liquid even when subjected to a pressure of 3600 atmospheres. This difference in behavior has led to the employment of different terms to distinguish the two classes of gases. Those which can be condensed to liquids by pressure alone are called *vapors*, while those which can not be so condensed are called gases, the last term being used in this narrower sense when it is wished to contrast these two kinds of behavior. The distinction is, however, one of comparatively small importance; for the properties of vapors and gases are essentially the same.

Liquids and solids, even under the ordinary conditions, do not show any uniform differences in behavior when the pressure upon them is varied, nor any regular differences in their degrees of compressibility or expansibility by heat, or in their densities. In a word, their *volume*-relations are substantially the same. Their distinguishing characteristic

is their difference in behavior with respect to changes in *form*. A substance is called a *liquid* when its form is greatly affected even by very slight external forces. A substance is called a *solid* when its form is appreciably changed only by the application of considerable external forces. Since the difference is one of degree, substances, like soft tar, which are in an intermediate state that can scarcely be designated either solid or liquid, are sometimes met with. Under ordinary conditions of pressure and temperature, however, it is relatively rare to find pure chemical substances which do not exhibit a marked difference with respect to stability of form in the two states of aggregation.

Solid substances are, moreover, sub-divided into two groups, designated crystalline and amorphous substances, which differ markedly in behavior and properties. One of the most important of these differences is that shown when the substances are sufficiently heated to cause them to pass into the liquid state. A *crystalline* substance, like ice, when heated, retains the stability of form characteristic of solid substances until a definite temperature is reached, at which it becomes liquid and undergoes at once a decided change in its properties; that is, a crystalline substance possesses a definite melting-point. An *amorphous* substance, on the other hand, like glass, when heated, gradually loses its stability of form and passes over into the liquid state continuously, that is, without undergoing at any temperature a sudden change in properties. An amorphous substance has no definite melting-point, but gradually softens as the temperature rises. The two groups of substances when in the form of homogeneous masses differ also in the following important respect. It is always true that some of the properties of homogeneous crystalline bodies (the so-called crystals) are different in different directions through the crystals, but all the properties of homogeneous amorphous bodies are the same in all directions. For example, nearly a third more tensile force has to be applied in

order to lengthen by a definite amount under corresponding conditions a piece of rock-salt in the direction of one of its so-called crystallographic axes than in a direction making an angle of 45° with these ; glass, on the contrary, is extended with equal readiness in all directions.   But, since extremely small crystalline particles may be irregularly aggregated to form an apparently homogeneous body, which would not exhibit difference of properties in different directions, this characteristic is not, from a chemical standpoint, as satisfactory a criterion of crystalline substances as their definiteness of melting-point.

Solid and liquid substances are also naturally subdivided, on the basis of certain other differences in properties, into two groups, known as metallic and non-metallic substances.   Although here again the differences are those of degree rather than of kind, and although a few substances occupy an intermediate position, yet in the great majority of cases the differences in properties are so marked as to make the distinction one of some importance.   A *metallic substance* is a substance which transmits light only through extremely thin layers and conducts electricity readily without undergoing any other changes than those produced by a rise in its temperature.   A *non-metallic substance* is one which transmits light through much greater thicknesses and either does not conduct electricity with any degree of readiness, or if it does conduct it, undergoes an attendant change in chemical composition.   Thus a centimeter-cube of copper allows electricity to pass through it freely and undergoes thereby only a rise of temperature ; on the other hand, one of rock-salt at the ordinary temperature allows scarcely any electricity to pass through it ; and though it can be made to conduct fairly readily by sufficiently raising its temperature or dissolving it in water, the passage of electricity through it is then attended by a partial decomposition into chlorine and sodium, or into chlorine, sodium hydroxide, and hydrogen.

Still another physical state of importance is that in which two or more different substances are so intimately mixed with one another that the masses of one or all of them become subdivided into minute particles which are uniformly distributed throughout the whole volume. Such intimate mixtures are designated by different names according to the degree of heterogeneity which they exhibit. If the particles of one of the components of the mixture are large enough to be seen by the eye with the aid of the best microscope, the mixture is called a *suspension* when the visible particles are those of a solid substance, and an *emulsion* when the visible particles are those of a liquid substance. When the particles are of such a size that the mixture exhibits no indication of heterogeneity under the best microscope, but nevertheless affects a beam of ordinary light thrown into it in the same way as fine suspensions affect it, namely, causes the beam to become scattered and the light to become polarized, the mixture is called a *colloidal* or *pseudo-solution*. Finally, if the particles are so small that no indication of heterogeneity can be detected by any physical instrument (even by a microscope or polariscope), the mixture is called a *solution*. Thus, the intimate mixture formed by agitating finely divided clay with water is a suspension, that made by violently shaking a little olive oil with water is an emulsion, that prepared by passing hydrogen sulphide into a boiling solution of arsenious oxide is a colloidal solution, and that made by adding salt to water is an ordinary solution. Such mixtures may be gaseous, liquid, or solid; but liquid mixtures are the most important.

The various kinds of mixtures which have just been described can in many cases be separated into their components by enclosing them within suitable porous walls or membranes and exerting a pressure upon them. Walls which permit the passage of one component of a mixture, but prevent entirely that of the other component, are called *semipermeable walls*. Different kinds of semiper-

meable walls must, however, be employed for the separation of the components of suspensions, colloidal solutions, and ordinary solutions, and this fact furnishes another basis for the differentiation of these three kinds of mixtures. Thus, filter paper will usually separate solid particles from a liquid in which they are suspended; but parchment or animal membranes must be employed for the separation of the components of colloidal solutions; and specially prepared semipermeable walls, such as are produced by the deposition of precipitates like copper ferrocyanide in the pores of unglazed porcelain, must be used for resolving ordinary solutions, like those of salt or sugar in water, into their constituents.

When the concentration of one component of a solution of two substances greatly exceeds that of the other component, the solution is said to be *dilute* with reference to the latter. In such a case, the component present in large amount is called the *solvent*, the one present in small amount, the *solute* or *dissolved substance*. If the concentration of neither component greatly exceeds that of the other, the solution is *concentrated* with respect to either component, and either may be designated the solvent or solute according to the relations under consideration. In the case of colloidal solutions, the substance which possesses the larger particles is called the *colloid*, and the other component is called the *solvent*.

Another term, which expresses from a different point of view the degree of heterogeneity of bodies, and which is much employed in considerations relating to their equilibrium, will be here defined. Heterogeneous bodies in a state of equilibrium are considered to consist of a number of parts which are differentiated by the possession of distinct sets of properties, and by their separation from one another by sharp physical boundaries, each part being characterized by uniformity in properties throughout its extent. These physically distinct parts are called *phases*. Thus, ice

and water, water and water-vapor, or salt and its saturated
aqueous solution, when existing together, constitute two
distinct phases. A body consisting of ice, a solid salt, an
aqueous solution of the salt, and water-vapor consists of
four phases, two of which are solid, one liquid, and one
gaseous; a body composed of liquid benzene and water
consists of two phases, both of which are liquid; one com-
posed of hydrogen, oxygen, and liquid water, consists also
of two phases, one of which is gaseous and the other liquid;
but one composed of hydrogen, oxygen, and water-vapor,
consists of only a single (gaseous) phase. It is to be noted
that the terms homogeneous, heterogeneous, and phase, are
always used in a physical sense, entirely without reference
to the number of chemical substances that may be present.

9. **Chemical Substances and Mixtures.** — Most, but
not all, of the numerous substances met with in nature, or
produced artificially, can be resolved by certain kinds of
processes which have been found suitable for the differen-
tiation of substances in the manner to be now considered,
into parts or fractions possessing properties different from
those of the original substances. A substance which can
not be resolved by such processes into component sub-
stances with different properties is called a *chemical sub-
stance*, or often simply a *pure substance*. All substances
which can be so resolved are called *mixtures;* for they can
be produced by mixing pure chemical substances. In ac-
cordance with these definitions, the method to be employed
for distinguishing chemical substances from mixtures con-
sists in submitting the material to various processes of
fractionation — that is, to operations which result in divid-
ing it into separate parts or fractions, and in then determin-
ing whether or not the properties of the different fractions
are identical. If identical, the material is probably a pure
substance: it may, however, be a mixture which the proc-
esses of fractionation employed have failed to separate into
the substances composing it. On account of this last pos-

sibility, as many distinct methods of fractionation as possible must be resorted to, and only if the fractions obtained by all methods are identical in properties, is the material to be regarded as a pure chemical substance. If the fractions are not identical, the material is probably a mixture: it may, however, be a pure substance which the processes of fractionation employed have converted in part into a different chemical substance. In order to avoid an erroneous conclusion from this source, only those processes of fractionation should be employed which have been shown by experience not to give rise as a rule to chemical transformations.

A more definite statement than that just made, of the character of the processes suitable for distinguishing chemical substances from mixtures can not be formulated, since the processes that must be applied vary greatly with the nature of the material. Some specific illustrations of the processes of fractionation commonly employed in the laboratory for determining the chemical purity of substances may, however, be presented. If the material is solid, it may be suspended in liquids of varying specific gravity in which it is insoluble, it may be partially melted, it may be treated with solvents in such quantity that only a portion is dissolved, or it may be completely dissolved and caused to crystallize from the solvent in separate portions by cooling or evaporation. If the material is liquid, it may be fractionated by partial freezing or partial volatilization, or by dialysis. If the material is gaseous, it may be resolved into fractions by causing it partially to diffuse through porous walls, or by treating it with liquid solvents in insufficient amount to dissolve the whole of the gas and expelling the dissolved part from the solvent by decrease of pressure or rise of temperature. On the other hand, processes involving the exposure of the substance to a high temperature (like the distillation of a difficultly volatile substance), the subjection of it to the action of an electric current or discharge, or the treatment of it with solvents of great chemi-

cal activity (like acids or bases), are not suitable ones for attaining the end in question.

The properties employed for determining the identity of the various fractions are any quantitative ones which can be conveniently measured, such as chemical composition, melting-point, boiling-point, specific gravity, crystalline form, spectrum, etc.

Although the above described means of distinguishing mixtures and chemical substances is the one which is usually first employed by the investigator and is one which in almost all cases leads to a correct conclusion, it is nevertheless somewhat indefinite and not always decisive; for some substances which in other respects behave like pure chemical compounds, are so unstable that even the ordinary processes of fractionation cause their decomposition; and, on the other hand, some mixtures consist of substances so similar in properties that such processes fail to effect separation. Other characteristic differences which have been found to exist between mixtures and chemical substances of known character must therefore be considered. One such characteristic difference of importance is that the specific properties of mixtures are at least approximately *additive*, that is, approximately the average of the properties of the substances into which they can be separated, while many of the properties of pure chemical substances seem to bear scarcely any relation to those of their decomposition-products. A *chemical substance* may, therefore, also be defined as a substance many of whose properties are not even approximately the average of the properties of the substances into which it can be resolved by *any* method whatever.

For example, water can be decomposed by the electric current into hydrogen and oxygen; but its properties are not in the least similar to those of these two gases. On the other hand, a mixture of hydrogen and oxygen, though separable into its component substances only imperfectly and

with difficulty, has specific properties which are the aver-
age of those of the two separate gases. If sugar is sub-
mitted to distillation it is resolved into distinct parts, namely,
into a black solid, a brown liquid, and a colorless gas; but
it would be obviously incorrect to conclude from this fact
that the sugar was a mixture, for most of its properties are
not in the least related to those of the fractions into which
it has been resolved. Similarly, if metallic sodium is
treated with an amount of water insufficient to dissolve it,
a gas and a white solid result, whose properties differ utterly
from those of the original metal; it is, therefore, clear that
the process has resulted in chemical decomposition and is
not a suitable one for determining the purity of the sodium.
The last two examples are of an extreme character, since
in each case the decomposition-products differ so markedly
from the original substance, and since decomposition of a
large part or of all of the original substance takes place.
In some cases a careful investigation is necessary, in order
to distinguish the effect of a slight decomposition from
that of an impurity originally present.

In distinguishing mixtures from pure chemical sub-
stances, it is best to apply in any doubtful case both of the
criteria which have been described; that is, first to deter-
mine whether the substance can be resolved into fractions
with different properties by the commonly employed proc-
esses of fractionation, and then to determine whether the
properties of the original substance are additive with respect
to those of these fractions: if not additive, the method of
fractionation employed must be rejected as unsuitable for
attaining the end in view.

A third, important, though not sufficient, criterion of
a pure chemical substance is furnished by its conformity
with the laws relating to elementary composition, which
have been proved to hold true in the case of all substances
determined to be pure by the two methods already described.
These laws and their value as a means of distinguishing
chemical substances and mixtures are considered below.

Since the properties of all substances vary to a greater or less extent with the temperature and pressure, and since the identity of two substances can be established only by comparing their properties under the same conditions, the question arises, whether a definite portion of matter is to be regarded as the same chemical substance, when it exists in different physical states. That pure chemical substances are sometimes transformed into other chemical substances merely by variations of temperature and pressure is proved by the fact that they sometimes become mixtures ; thus, the vapor produced when solid ammonium chloride is heated can be shown by diffusion experiments to be a mixture of ammonia and hydrochloric acid gases. Even when a mixture does not result, it is evidently somewhat arbitrary to attribute a radical change in the properties of a substance to a change in its physical state rather than to a complete transformation of it into another chemical substance. Nevertheless, the practice which is commonly followed is to regard pure substances which pass over into one another completely and reversibly by variations of temperature or pressure as the same chemical substance. Thus, ice, water, and water-vapor, or rhombic sulphur, monosymmetric sulphur, liquid sulphur, and sulphur-vapor, are designated different physical states of the same substance. Ozone and oxygen, or paracyanogen and cyanogen, are, on the other hand, appropriately regarded as distinct substances ; for, though increase of temperature will convert the former into the latter, the oxygen so produced can not be changed back to ozone, or the cyanogen to paracyanogen, merely by restoring the original temperature.

10. **Elementary and Compound Substances.** — When chemical substances are brought together, or are subjected, alone or mixed, to a high temperature or to certain other influences, a change often takes place which results in the formation of new chemical substances. When the weight of one of the new substances formed is less than that of the substance from which it is produced, and the change is

known to be complete, the original substance is said to have been decomposed. Now, almost all chemical substances can be made to undergo some change of this kind, but a relatively small number have been discovered which do not give rise in any complete change that they undergo to a new substance whose weight is less than that of the original substance. These substances, which every means at our disposal has failed to decompose, are called *elementary substances*. All other chemical substances can directly or indirectly be produced from, or resolved into, these elementary ones ; they are therefore considered to be composed of them, and are called *compound substances*, or simply *compounds*.

11. Law of the Conservation of the Elements.— Certain other important limitations in regard to the transformation of chemical substances into one another are also to be considered in this connection. In the first place, it is found that, although in certain cases one elementary substance is transformed into another, for example, oxygen into ozone or diamond into graphite, yet there exist about eighty elementary substances or groups of elementary substances which are not transformed into one another by any process whatever, whether direct or indirect. Thus the innumerable efforts of the alchemists and the experiments of modern investigators with their vastly greater resources have alike failed to transform copper into gold, lead into silver, or chlorine into oxygen, even with the help of indirect processes or of those of a most energetic character. Correspondingly, compounds or mixtures of them are never transformed except into such other compounds or mixtures as can be decomposed into the same elementary substances as can the original compounds ; thus a mixture of lead chloride and potassium bromide is readily transformed into one of lead bromide and potassium chloride, but it is impossible to prepare from such a mixture a silver salt or an iodide. Furthermore, when two or more elementary substances unite to form compounds, or mixtures of them, even

though almost all of the properties of the elementary sub-
stances may have disappeared, it is always possible by suit-
able methods to get back exactly the same amounts of each
of the elementary substances as originally entered into the
compounds.

These facts have led to the assumptions that there
exist constant unchangeable amounts of a comparatively
small number of distinct kinds or forms of matter, and that
elementary substances contain only one of these, while com-
pound substances contain two or more of them.   These
distinct kinds or forms of matter are called *elements;* and
the empirically established principle that they are neither
created nor destroyed by any process whatever is appropri-
ately called the *Law of the Conservation of the Elements.*

The abstract conception denoted by the word element
will be seen to have a significance distinct from that of the
concrete term elementary substance.   Thus it would be inap-
propriate to speak of the existence of elementary substances
in compounds ; for hardly any of their properties are, as a rule,
exhibited by the compounds.   Nor are the properties of
either elementary or compound substances determined solely
by the elements contained in them ; their properties are
rather to be regarded as the result of the temporary associa-
tion with the element or elements of quantities of energy.
Moreover, it is not to be inferred from the use of the ex-
pression "distinct kinds or forms of matter" in the defini-
tion of the elements that there exist eighty or more
entirely unrelated *ultimate* realities, for it might be that the
elements represent only certain permanent associations of
matter and energy : the ultimate nature of the elements,
like that of matter, is entirely unknown.   The concept of
elements and the assumption of their existence in both
elementary and compound substances furnish convenient
means, avoiding much circumlocution, of expressing the fact,
stated in the first paragraph of this section, that the quantity
of any elementary substance which can be obtained from

any body is constant, whatever changes that body, or the chemical substances composing it, may undergo. The term element further implies, to be sure, the permanent existence of a real thing, whose nature is unknown, that gives rise to this constancy. Thus its significance is entirely similar in kind to that of the term matter.

A list of the well-established elements, with the symbols by which they are represented, is given in § 16. Others undoubtedly exist, for new ones are frequently discovered; and some few of those now regarded as such may prove to be mixtures or compounds. Indeed, it is impossible to say that some process may not be discovered by which all the present elementary substances can be resolved into simpler substances. The existence, however, of certain similarities and relationships between the properties of the various elementary substances and of certain systematic differences between their properties and those of compound substances, and the *relative* permanence of the elements (even if it should prove not to be an absolute one, as all our experience thus far indicates it to be), furnish conclusive proof that all the well-known elements are substances of the same order, and of an order distinct from that to which our present compound substances belong. This is not the place to present in detail the facts which have led to this conclusion, but it may be mentioned that among the most important of them are the relationships between the properties of elementary substances which are brought out by the so-called Periodic System, and the uniformity in the heat-capacities of solid elementary substances which is expressed by the Law of Dulong and Petit.

12. Law of Definite Proportions. — Investigations of the elementary composition of substances have proved that a series of pure chemical compounds containing the component elements in continuously varying proportions by weight does not exist, but that there exists only a finite number of compounds, each of perfectly definite composi-

tion. Chemical substances obtained from different sources or by different methods are either absolutely identical in composition, or they differ from one another by considerable amounts. When a chemical substance changes in composition, even though the change may take place gradually, it is never possible to isolate by the methods illustrated in § 9 a series of chemical substances varying continuously in composition, but the change results in the formation of a single new substance (or a small number of new substances) differing markedly in composition from the original substance (and from one another). There is never a gradual transition in the composition of chemical compounds, but always a sharp, sudden change. These statements are an expression of what is known as the *Law of Definite Proportions.*

For example, when salt is prepared from sodium hydroxide and hydrochloric acid, it is not found that its composition is in any way dependent on the proportions of the ingredients taken or on the conditions of temperature or concentration; the product is not found to contain a larger proportion of chlorine when an excess of hydrochloric acid is used, nor of sodium when an excess of sodium hydroxide is employed. When zinc is burnt, there are no intermediate products between it and its oxide; but if the combustion is interrupted before its completion, the product is found to be a mixture of unchanged zinc and its oxide, not a single chemical compound intermediate in composition and properties.

The Law of Definite Proportions, which had before been tacitly recognized, was energetically disputed at the beginning of the last century, but was soon established by careful analyses with as great a degree of accuracy as the state of analytical chemistry then permitted. More recently it was suggested that the composition of chemical compounds might still be variable within narrow limits, but the experiments of Stas, made with a view of testing this supposition,

showed that the variations, if any exist, are less than the unavoidable experimental errors of analysis. For he determined, in the case of five distinct samples of ammonium chloride obtained from entirely different sources or by different methods of purification, the weight of silver which, after solution in nitric acid, sufficed to precipitate a definite weight of the chloride, and found the extreme variations in the ratio of these weights to be less than one ten-thousandth part of its value.

It may be added that *all* the properties of pure chemical substances exhibit the same definiteness and discontinuity as does their elementary composition, and that the differentiation of chemical substances and mixtures finds its experimental justification in the fact that there exist a limited number of substances with perfectly definite properties of such a relatively high degree of stability towards resolving agencies that they can be prepared with the help of such agencies from a variety of materials. The Law of Definite Proportions and the principle of the definiteness of properties in general are therefore involved in the definitions of chemical substances given in § 9.

13. The Law of Multiple Proportions. — Investigations have also shown that certain simple relations exist between the quantities of the elements combined with one another in different chemical compounds. These are commonly expressed in the form of two principles, called the Law of Multiple Proportions and the Law of Combining Weights.

The *Law of Multiple Proportions* is as follows : *When one element combines with another in several proportions to form different chemical compounds, the quantities of the one element which in the several compounds are combined with the same quantity of the other element, stand to one another in the ratio of small whole numbers.*

For example, in one of the two known compounds of carbon and oxygen, 16 parts by weight of oxygen, and in

the other 32 parts of it, are combined with 12 parts of car-
bon. Five compounds of nitrogen and oxygen exist, in
which the quantities of the latter combined with any defi-
nite quantity of the former are to one another exactly as
1 : 2 : 3 : 4 : 5. Sometimes, however, especially in the case
of compounds of the element carbon, the ratio is much less
simple; thus, in the two hydrocarbons, naphthalene and
anthracene, the relative quantities of hydrogen combined
with one gram of carbon are as 28 : 25.

14. **The Law of Combining Weights.** — Careful
investigations of the quantitative elementary composition of
chemical substances have shown that to the elements in-
dividually can be assigned definite numerical values which
accurately express the weights of them, or small multiples
of the weights of them, which are combined with one
another in all chemical compounds. Such numerical values
are called the combining weights of the elements. Since
they are essentially relative quantities, greater definiteness
can be attained by adopting a definite weight of some one
element as a standard of reference. Adopting 16 grams of
oxygen as the standard in accordance with what is probably
the best practice, the *combining weight* of an element is
defined to be that weight of it which combines with 16
grams of oxygen, or with some small multiple or submultiple
of 16 grams of oxygen. And with the help of this definition
the principle involved in the preceding statement, and known
as the *Law of Combining Weights*, can be concisely expressed
as follows : *Elements combine with one another only in the
proportions of their combining weights or of small multiples
of them.*

This law may be illustrated by citing the experiments
of Stas which have furnished the most exact confirmation
of it. By dissolving carefully purified silver chlorate in
water, reducing it to the insoluble chloride, and testing the
solution for an excess of silver and chlorine, he proved that
the ratio of the quantities of these two elements in silver

chlorate does not differ from the ratio of them in silver
chloride by more than one ten-millionth part of its value,
which was the limit of delicacy of the tests. Similar ex-
periments were made with similar results with silver bro-
mate and iodate. Careful determinations were also made, by
indirect methods, of the quantities of silver combined with a
definite quantity of oxygen in these three salts and in silver
sulphate. The quantities combined with 16 grams of oxygen
were found to be as follows :

In silver chlorate . . . . 35.980 grams.
In silver bromate . . . . 35.974 grams.
In silver iodate . . . . 35.979 grams.
In silver sulphate . . . . 53.963 $= \frac{3}{2} \times$ 35.976 grams.

It will be seen that the numerical values adopted as
the combining weights are, so far as the Law of Combining
Weights is concerned, arbitrary in two respects : first, be-
cause it is necessary to adopt an arbitrary standard of refer-
ence ; and secondly, because, in the case of each element,
some arbitrary multiple of the value obtained by the analysis
of any one of its compounds must be selected. A decision
in regard to both of these matters must be reached by
general agreement, but it should be such as will secure
the greatest degree of permanence in the system of com-
bining weights adopted, and will furnish the simplest ex-
pression of the elementary composition and allied proper-
ties of chemical substances.

The reasons for adopting 16 grams of oxygen as the
standard of reference may first be briefly considered. In-
stead of oxygen, hydrogen was for a long time almost uni-
versally employed as the standard substance, and it still
continues to be used to a considerable extent. It has the
advantage of possessing the smallest combining weight, so
that a unit-weight (one gram) of it can be adopted as the
standard weight without making it necessary to express the
combining weights of other elements in the form of incon-

venient fractions. Hydrogen has also another, more impor-
tant advantage over oxygen, by reason of the fact that, in
comparing the quantities of different chemical substances
which enter into reactions with one another, it is, as a rule,
simpler and more in accordance with actually existing rela-
tions to use as the basis of comparison the quantity of hydro-
gen rather than the quantity of oxygen involved in the
reactions in question or in similar ones, — a fact which will
come into more prominence in connection with the defini-
tion of equivalent weights (§19). Oxygen, on the other
hand, has the great practical advantage that the combining
weights of almost all the other elements have been actually
determined either from the composition of their oxides or
from that of their compounds with the halogens, the com-
bining weights of which latter have themselves been estab-
lished by determining the relative quantities of halogen and
oxygen present in compounds containing both of them (see
§ 15). The experimental basis of the system of combining
weights is therefore oxygen, and not hydrogen; and if the
latter were adopted as the conventional basis, it would be
necessary to calculate the values over to the hydrogen stand-
ard with the help of the ratio between the combining weights
of hydrogen and oxygen. Every new, more accurate deter-
mination of this ratio would then involve a corresponding
change in the values of almost all the other combining
weights: moreover, until very recently, a great degree of un-
certainty has existed in regard to the exact value of this ratio;
and, even at the present time, it is not known as accurately
as the ratio of the combining weights of some of the other
elements to that of oxygen. For these reasons, although
some difference of opinion does still exist in regard to the
relative importance of the different advantages which the
two elements possess, it seems at present to be the best
practice to refer the combining weights to oxygen, and this
practice will be adhered to throughout this work. The
principal reasons for adopting 16 grams of this element

(instead of one gram, for example), as the standard of reference, are : first, that it involved a comparatively slight change in the values of the combining weights from those prevailing some years ago, when the commonly employed hydrogen standard was to be replaced ; and second, that the combining weight of hydrogen is still not far from unity (1.0075, according to the most accurate determinations), so that to some extent at least — thus, in cases where the greatest accuracy is not required — the advantages of the hydrogen standard are retained.

In regard to the adoption of definite multiples of the values obtained by chemical analysis, it can only be stated at this point that investigators, guided by certain theoretical considerations, have reached a substantially unanimous agreement, and have succeeded in establishing a system of combining weights which not only serves to express in a simple manner the elementary composition of chemical substances, but also forms a highly satisfactory basis for the development of the knowledge of their properties and transformations. It should be distinctly understood, however, that the conception of combining weights does not involve the use of these particular multiples or of any definite multiples of the analytical values ; and if, for the sake of convenience, such are adopted, it must be fully realized that the multiplying factors are arbitrary ones in the sense that they can not be determined by quantitative analyses of chemical substances.

The method of calculating combining weights from analytical data and the arbitrariness of adopting a definite multiple may be illustrated by examples. Syntheses of carbon dioxide from its elements have shown that it contains 27.27 per cent. of carbon and 72.73 per cent. of oxygen. The combining weight of carbon referred to that of oxygen taken as 16.00 is therefore $\frac{27.27}{72.73} \times 16.00 = 6.00$, or any small multiple or submultiple of this value. Carbon monox-

ide is found to contain 42.50 per cent. of carbon and 57.50 per cent. of oxygen, from which it follows that the combining weight is $\frac{42.50}{57.50} \times 16.00 = 12.00$, or any small multiple or submultiple of it. Finally, alcohol is found by analysis to contain 52.12 per cent. of carbon, 34.75 per cent. of oxygen, and 13.14 per cent. of hydrogen; the combining weight of carbon is, therefore, $\frac{52.12}{34.75} \times 16.00 = 24.00$, or any small multiple or submultiple of it. It would evidently be entirely arbitrary to select as the combining weight a particular one of the three values calculated directly from the composition of these different compounds.

It should be added that the term combining weight is often used in a similar sense in connection with compound substances. The *combining weight of a compound* is defined to be that weight of it which contains such weights of the component elements as are their combining weights or small multiples of them.

In closing this consideration of the Law of Combining Weights attention may be called to the fact that the Law includes as special cases the Laws of Definite and Multiple Proportions. It is therefore the general law relating to the elementary composition of pure chemical substances.

15. Determination of the Combining Weights. — The combining weights of the elements are constants of so great importance that a general knowledge of the way in which they have been determined is desirable. A partial outline of the extensive and highly accurate series of determinations which were made by Stas in the years 1860 to 1864 will therefore be presented. This will not only serve to illustrate the general character of the methods of determining combining weights, but will also give a good idea of the experimental basis upon which the commonly employed system of combining weights in large part rests.

In determining the combining weight of silver the fol-

lowing five methods were employed : 1. A known weight of pure potassium chlorate was converted, in some experiments by ignition, and in others by treatment with hydrochloric acid, into potassium chloride, and the weight of the latter compound formed accurately determined. The combining weight of the potassium chloride referred to oxygen is then evidently given by the proportion, the weight of the potassium chloride obtained is to the difference between the weight of the potassium chlorate taken and that of the potassium chloride obtained as the combining weight of potassium chloride is to the combining weight of oxygen (assumed to be 16 or some multiple of it). The quantity of oxygen in potassium chlorate is assumed to be 48, that is, three times the combining weight, since it has been found that the composition of chemical compounds is, on the whole, more simply expressed when this assumption is made. Stas used 801.4780 grams of potassium chlorate in eight experiments, which gave, upon reduction, 487.6605 grams of potassium chloride, whence follows a value of 74.5902 ± 0.0045 for the combining weight of the latter. (The quantity following the ± sign signifies here, as usual, the probable error of the result.) Weighed quantities of potassium chloride and metallic silver were then dissolved in water and dilute nitric acid, respectively, and the relative quantities of the two ·substances which exactly precipitated each other determined. The sum of the amounts of potassium chloride used in twenty-three experiments was found to be 147.70775 grams, and to this 210.85508 grams of silver were found to correspond ; and from the proportion, 147.70775 : 210.85508 : : 74.5902 : the combining weight of silver, follows for the last named quantity the value 107.9401 ± 0.0058.

2. Weighed quantities of silver chlorate were dissolved in water and reduced by means of sulphurous acid to silver chloride. The composition of the latter was also determined, first, by heating silver in chlorine gas, and second, by dis-

solving it in nitric acid and precipitating with hydrochloric acid or ammonium chloride.

3. Silver bromate was reduced in the same way to silver bromide, in order to determine the combining weight of the latter with reference to that of oxygen. The composition of the silver bromide was determined by a *complete synthesis;* that is, the weights of silver and of bromine which combine with each other were determined, as well as the weight of their product. The fact that the last weight was almost exactly equal to the sum of the weights of the elements taken is an almost conclusive proof of the purity of all the substances, and of the accuracy of the experiments.

4. The combining weight of silver iodide was similarly determined by reducing silver iodate with sulphurous acid solution to silver iodide, and also by a *complete analysis* of the iodate, which consisted in decomposing weighed quantities of it by heat and weighing the quantities of silver iodide and oxygen produced. The composition of silver iodide was determined by a complete synthesis.

5. Silver sulphate was reduced to metallic silver by continued heating in a stream of hydrogen gas. The composition of silver sulphide was also determined.

The results obtained by the five methods which have been just described are shown in the following table. The numbers are the combining weights of the substances whose formulas are given at the beginning of the separate lines.

1. KCl from $KCl : KClO_3$ $= 74.5902 \pm 0.0045$
2. AgCl from $AgCl : AgClO_3$ $= 143.3940 \pm 0.0064$
3. AgBr from $AgBr : AgBrO_3$ $= 187.8759 \pm 0.0237$
4. AgI from $AgI : AgIO_3$ $= 234.7907 \pm 0.0095$
5. Ag_2S from $\begin{cases} 2Ag : Ag_2S \\ 2Ag : Ag_2SO_4 \end{cases}$ $= 247.9074 \pm 0.0215$

1. Ag from Ag : KCl   = 107.9401 ± 0.0058
2. Ag from Ag : AgCl   = 107.9406 ± 0.0049
3. Ag from Ag : AgBr   = 107.9233 ± 0.0140
4. Ag from Ag : AgI   = 107.9371 ± 0.0045
5. Ag from 2Ag : Ag_2S = 107.9270 ± 0.0090

Mean = 107.9376 ± 0.0037

From the results just tabulated the combining weights of chlorine, bromine, iodine, and sulphur can be directly obtained by subtracting the mean value of the combining weight of silver from the combining weight of the corresponding silver compound, and that of potassium, by subtracting that of chlorine from the combining weight of potassium chloride. The combining weights of the first four elements can also be computed from the mean value for silver and the composition of their compounds with it. The values obtained by a combination of these two methods are :

$$Cl = 35.4529 ± 0.0037$$
$$Br = 79.9628 ± 0.0032$$
$$I = 126.8640 ± 0.0035$$
$$S = 32.0626 ± 0.0042$$
$$K = 39.1361 ± 0.0032$$

In a similar manner the combining weights of other elements have been determined. One of the most common processes consists in preparing the chloride or bromide of the element, and in determining the proportion of chlorine or bromine in it by precipitation with silver nitrate.

16. **Numerical Values of the Combining Weights.** — The following table contains the names of the well-established elements, the symbols by which they are commonly represented, and the most probable values of their combining weights, which have been derived through a critical consideration of the results of all the determinations which have been made up to the present time. Those multiples of the analytical values are given which are now commonly em-

ployed by chemists, and which, by reason of certain theo-
retical considerations connected with them, are designated
atomic weights. The values are referred to the oxygen
standard, the combining weight of this element being as-
sumed to be 16.000. Such a number of figures is retained
that the figure before the last is probably not uncertain by
as much as one unit. Columbium and niobium, beryllium
and glucinum, are merely different names for the same
elements. As no compounds of the recently discovered
gaseous elements, argon, helium, krypton, neon, and xenon,
have been prepared and analyzed, no combining weights
are assigned to them in the table.

TABLE OF COMBINING AND ATOMIC WEIGHTS.

Aluminum	.	Al	27.1	Neodymium.	. Nd	143.6
Antimony.	.	Sb	120.0	Neon . . .	. Ne	. . .
Argon . .	.	A	. . .	Nickel. . .	. Ni	58.70
Arsenic	. .	As	75.0	Niobium . .	. Nb	94.
Barium	. .	Ba	137.43	Nitrogen . .	. N	14.04
Beryllium.	.	Be	9.1	Osmium . .	. Os	190.8
Bismuth	. .	Bi	208.	Oxygen . .	. O	16.000
Boron . .	.	B	11.0	Palladium .	. Pd	106.5
Bromine	. .	Br	79.955	Phosphorus .	. P	31.0
Cadmium .	.	Cd	112.3	Platinum . .	. Pt	195.2
Cæsium	. .	Cs	132.9	Potassium	. . K	39.14
Calcium	. .	Ca	40.1	Praseodymium .	Pr	140.5
Carbon . .	.	C	12.001	Rhodium . .	. Rh	103.0
Cerium . .	.	Ce	140.	Rubidium	. . Rb	85.44
Chlorine .	.	Cl	35.455	Ruthenium .	. Ru	101.7
Chromium	.	Cr	52.14	Samarium	. . Sm	150.
Cobalt . .	.	Co	59.00	Scandium	. . Sc	44.
Columbium .		Cb	94.	Selenium . .	. Se	79.2
Copper . .	.	Cu	63.604	Silicon . . .	. Si	28.4
Erbium	. .	Er	166.	Silver . . .	. Ag	107.93
Fluorine .	.	Fl	19.05	Sodium . .	. Na	23.05
Gadolinium .		Gd	156.	Strontium	. . Sr	87.68
Gallium	. .	Ga	70.0	Sulphur . .	. S	32.065
Germanium .		Ge	72.5	Tantalum	. . Ta	183.
Glucinum .	.	Gl	9.1	Tellurium	. . Te	127.5
Gold	. . .	Au	197.3	Terbium . .	. Tb	160.
Helium	. .	He	. . .	Thallium . .	. Tl	204.15
Hydrogen .	.	H	1.0075	Thorium . .	. Th	233.
Indium	. .	In	114.	Thulium . .	. Tu	170.
Iodine . .	.	I	126.85	Tin	. Sn	119.0
Iridium	. .	Ir	193.0	Titanium . .	. Ti	48.17
Iron . . .	.	Fe	55.9	Tungsten	. . W	184.
Krypton	. .	Kr	. . .	Uranium . .	. U	238.5
Lanthanum .		La	138.5	Vanadium .	. V	51.4
Lead	. . .	Pb	206.92	Xenon	. . . X	. . .
Lithium	. .	Li	7.03	Ytterbium	. . Yb	173.
Magnesium .		Mg	24.36	Yttrium . .	. Y	89.0
Manganese .		Mn	55.02	Zinc . . .	. Zn	65.40
Mercury	. .	Hg	200.0	Zirconium	. . Zr	90.6
Molybdenum		Mo	96.0			

17. Elementary Composition as a Means of Distinguishing Chemical Substances from Mixtures. — Since pure chemical substances contain the elements in quantities that are proportional to their combining weights or small multiples of them, while mixtures may contain the elements in any proportion, it is evident that a knowledge of the quantitative elementary composition of a substance is of assistance in determining whether it is a pure compound or a mixture. It is not true, however, as may seem at first to be the case, that a correct decision can always be reached by this method. For this there are two reasons. The first is that the analyses of substances proved to be pure by the two methods described in § 9 have shown, that, while in the case of the compounds of almost all the elements the small whole numbers by which the combining weights must be multiplied in order to express the composition correctly, seldom exceed a few units in value, yet in the case of some of the compounds of a few elements, notably carbon, the values of these multiplying factors are so large, that, in view of the unavoidable analytical errors, the elementary composition is of no assistance in distinguishing such compounds from mixtures. The second reason is that experience has shown that *isomeric* substances exist, that is, substances which, though distinct in some of their other properties, are identical in their elementary composition. It may be added that isomeric substances, like those of complex composition, are extremely common among the compounds of carbon, but are comparatively rare among those not containing this element.

Conformity in composition with that required by the Law of Combining Weights is therefore only an important indication, not a universally applicable criterion, of a pure chemical substance, while apparent non-conformity with it is a strong indication, but not conclusive evidence of a mixture. The indications are generally reliable in the case of the compounds of other elements than carbon, but very uncertain in the case of these.

Some examples of non-conformity with the Law may be presented. If a sample of rock-salt were found on analysis to contain, in combination with 35.45 grams of chlorine, 22.50 grams of sodium, instead of the 23.05 grams which its combining weight requires, the salt would be correctly pronounced a mixture. But if the pure substance stearine, which in reality contains the elements carbon, hydrogen, and oxygen, in the ratio of 57 combining weights of the first to 110 of the second to 6 of the third, were accurately analyzed, and the same reasoning applied to the results, the erroneous conclusion that it also is a mixture might be drawn, on account of the apparent non-conformity in composition with the Law of Combining Weights.

It is evident from these considerations that, if the Law of Combining Weights is to apply to all chemical compounds, the restriction in the statement of it to the effect that the multiples of the combining weights of the component elements are small ones, must be broadly interpreted. It is nevertheless true, that the significance of these laws, both from an analytical and a theoretical standpoint, depends very largely on the fact that the integral factors involved do not exceed a few units in value in the case of a large proportion of compounds.

18. **Chemical Formulas and Chemical Equations.** — In order to express the gravimetric composition of compounds, the symbols of the elements are considered to represent their combining weights, and are written in sequence with such integers as subscripts as will make the resulting formulas express the proportions by weight of the elements in the compounds. Such formulas, which express nothing more than the results of analysis, are called *empirical formulas.* Thus, water is found to contain hydrogen and oxygen in the proportion of 1.0075 : 8, and since the combining weights of these elements are 1.0075 and 16, the empirical formula of water is H_2O.

In order to determine the formula of a compound from

its percentage composition, the percentage weight of each element is divided by its combining weight, and the resulting values, which evidently express the relative number of combining weights of the separate elements in the compound, are then multiplied by such a factor as will make them all whole numbers, or so nearly equal to whole numbers that the deviation is not greater than can be accounted for by the experimental error. This factor can commonly be obtained at once by inspection, especially if the relative values are first simplified by dividing them all by the smallest one of them.

For example, ferric oxide is found by analysis to contain 30.0 per cent. of oxygen and 70.0 per cent. of iron. The ratio of the number of combining weights of these elements in the compound is, therefore, $\frac{70}{56} : \frac{30}{16}$, or 1.250 : 1.875, or 1 : 1.5. The empirical formula is, therefore, Fe_2O_3. — An actual analysis of an organic substance by the ordinary method showed the following percentage composition: C : 51.60; H : 7.05; O : 41.35. Therefore the ratio of the number of combining weights is $\frac{51.60}{12.00} : \frac{7.05}{1.0075} : \frac{41.35}{16.00}$, or 4.30 : 7.00 : 2.58, or 1.67 : 2.71 : 1.00, or 5.00 : 8.13 : 3.00. Since the deviation from an integer of the calculated number of combining weights of hydrogen (8.13) would correspond to a variation of about 0.1 of a unit in its percentage weight (7.05), and since an experimental error of this magnitude is usual in such analyses, no significance is to be attached to the deviation, and the conclusion is to be drawn that the composition of the compound is represented within the experimental error by the empirical formula $C_5H_8O_3$.

In order, on the other hand, to calculate the percentage composition of a compound from its formula, the number of combining weights of each element (as shown by the subscripts in the formula) is multiplied by the corresponding combining weight itself, and each product is then divided by the sum of the products. The result gives evidently the fractional quantities of the various elements in the com-

pound. Thus the formula of cane sugar is $C_{12}H_{22}O_{11}$. The ratio of the weights of the elements contained in it is, therefore, $12 \times 12.00 : 22 \times 1.0075 : 11 \times 16.00$, or $144 : 22.2 : 176$; and the percentage of carbon is $\dfrac{100 \times 144}{144 + 22.2 + 176}$, or 42.08.

In order to express the relative quantities of substances that enter into and are produced by chemical transformations, their formulas are considered to represent not only the proportions by weight of the elements of which they are composed, but also absolute weights of the substances equal to the sum of the weights represented by the symbols of the elements in the formulas. This weight may be designated the *formula-weight* of the substance. Thus the formula of sulphuric acid, H_2SO_4, represents $(2 \times 1.0075) + 32.065 + (4 \times 16.000) = 98.080$ grams of sulphuric acid; and that of sodium hydroxide, $NaOH$, $23.050 + 16.000 + 1.008 = 40.058$ grams of sodium hydroxide. The formulas of substances involved in a definite *reaction* (that is, in a definite chemical transformation) are then written together in the form of an equation, each formula being preceded by such an integral coefficient as will make the equation express the relative quantities of the reacting substances. For example, the expression,

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O,$$
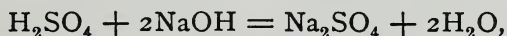
signifies that 98.080 parts by weight of sulphuric acid react with 80.115 parts of sodium hydroxide with the production of 142.165 parts of sodium sulphate and 36.030 parts of water.

It is evidently a simple matter to determine with the help of such equations the quantity of a product obtainable from a definite quantity of another substance. Two considerations which are apt to be overlooked by those unfamiliar with such calculations may be referred to, however. In the first place, it is of course essential that the formulas used in the calculations represent the composition of the

substances actually weighed; for example, the reaction be-
tween barium chloride and potassium sulphate is commonly
written as follows:

$$BaCl_2 + K_2SO_4 = BaSO_4 + 2KCl;$$
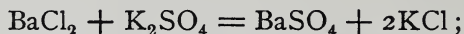
but, if pure crystallized barium chloride, which contains
water of crystallization, is the substance weighed out, its
formula, $BaCl_2.2H_2O$, and not the simpler one used in the
above equation, must be employed in the calculation.
Secondly, where one substance is converted into another by
a series of chemical reactions, it is not necessary to cal-
culate the quantities of the intermediate products formed,
but it suffices to compare the weights corresponding to the
formulas of the original and final substances; in such cases,
however, care must be taken to use in the calculation
those multiples of the formula weights which contain equal
weights of the common element.   For example, if it be
desired to find how much silver chloride is formed from a
given weight of chlorine, when the transformation takes
place in accordance with the equations,

$$H_2 + Cl_2 = 2HCl, \text{ and,}$$
$$AgNO_3 + HCl = AgCl + HNO_3,$$
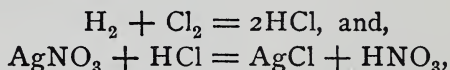
it is superfluous to calculate first the quantity of hydro-
chloric acid, and then that of silver chloride; for the lat-
ter is obtained directly from the ratio $2AgCl : Cl_2$ (not,
however, from the ratio $AgCl : Cl_2$).   If ferric oxide (Fe_2O_3)
is completely transformed, by the removal of oxygen in any
manner whatever, into ferroso-ferric oxide (Fe_3O_4), the
relative weights of the two substances are not expressed by
the simple ratio $Fe_2O_3 : Fe_3O_4$, but by the ratio $3Fe_2O_3 :
2Fe_3O_4$, since only in the latter case do the two formulas
represent quantities of the substances containing the same
amount of iron.

19. **Definition of Equivalent Weights.** — The equa-
tions used as examples in the last section illustrate the fact
that the relative weights of the substances involved in any

reaction are not necessarily the formula-weights, but are frequently small multiples of these. It is therefore highly desirable to have different terms for these different quantities, and it has become customary to designate the weights of substances which enter into reactions with one another, or take the place of one another in corresponding reactions, as *equivalent weights*. In giving definiteness to this term, the difficulty is met with that reactions exhibit some diversity of character, and that those weights of substances which are comparable with one another with respect to one kind of reactions may not be so with respect to other kinds. This difficulty is not serious, however, in the case of the metallic elements and their compounds ; for most of the reactions in which they are involved are included in one of two classes known respectively as metathetical reactions, and as oxidation-and-reduction reactions.

A *metathetical reaction* is one in which an element or group of elements in one compound changes place with some other element or group in another compound. All the reactions illustrated by equations in the preceding section are metathetical reactions, except the combination of hydrogen and chlorine. A *reaction of oxidation and reduction* is one in which oxygen or some acid-forming element or group, or hydrogen or some base-forming element or group, is taken away from one compound and added to another compound ; the compound which takes up oxygen or the acid-forming element or loses hydrogen or the base-forming element, is said to be *oxidized*, and the compound of which the reverse is true, to be *reduced*. The following equations represent reactions of oxidation and reduction, the substance which is oxidized being placed first in each case.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$
$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + KCl.$$
$$3PbS + 8HNO_3 = 3PbSO_4 + 8NO + 4H_2O.$$
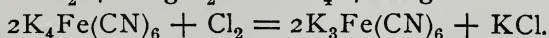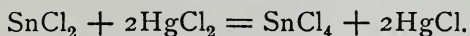
If now we recognize that in correspondence with these two important classes of reactions a substance may have

two different equivalent weights, and if we adopt a definite quantity of some substance as a standard of reference, the term equivalent weight becomes a fairly definite one. Since hydrogen is the element which always undergoes replacement in the important metathetical reactions in which acids or bases take part, and since it is also frequently involved in reactions of oxidation and reduction, it is most natural and convenient to adopt some quantity of it as the standard; and it is customary to select as this quantity its combining weight (approximately 1.0075 grams), which makes the latter identical with its equivalent weight, and makes 16 grams of oxygen the ultimate basis of the system of equivalent weights as well as of that of combining weights. The *equivalent weight* or *one equivalent* of a substance is then defined to be that weight of it which enters into a reaction of simple metathesis, or of oxidation and reduction, with one equivalent of hydrogen or with that weight of any other substance which itself reacts with one equivalent of hydrogen. Whether the hydrogen is in the form of the elementary substance or in that of one of its compounds, is immaterial. If the reaction under consideration is a metathetical one, the quantity just defined is called the *metathetical equivalent*, if one of oxidation and reduction, the *oxidation-equivalent*, of the substance.

The following examples will serve to illustrate these statements. One equivalent of any acid is evidently that weight of it which contains one equivalent of hydrogen capable of reacting with a base, and one equivalent of any base is that weight of it that neutralizes one equivalent of an acid. Thus, the formula-weights, 36.46 and 60.03 grams, of hydrochloric acid (HCl) and of acetic acid ($HC_2H_3O_2$) are also the equivalent weights of these substances, for these weights contain one equivalent (1.0075 grams) of replaceable hydrogen. The equivalent weight of sulphuric acid (H_2SO_4), on the other hand, is only one-half of its formula-weight (98.08 grams), that is, 49.04 grams. Simi-

larly, the equivalent weight of sodium hydroxide (NaOH) is identical with its formula-weight, while that of barium hydroxide (BaO_2H_2) is one-half, and that of ferric hydroxide (FeO_3H_3) one-third, of its formula-weight. The equivalent weight of silver nitrate ($AgNO_3$) is the same as its formula-weight, since that quantity precipitates one equivalent of hydrochloric acid; those of barium chloride ($BaCl_2$) and ferric chloride ($FeCl_3$) are one-half and one-third of their formula-weights respectively, since it is these quantities that are produced by the neutralization of one equivalent of hydrochloric acid by the corresponding bases, or since they react with one equivalent of silver nitrate.

In order to determine the oxidation-equivalent of a substance it is necessary to know into what other substance it is reduced or oxidized, and to consider how much hydrogen would be required to effect its reduction, or the same reduction of other substances which it itself is capable of effecting. Thus the oxidation-equivalent of ferric chloride with respect to its reduction to ferrous chloride ($FeCl_2$) is the weight corresponding to the formula $FeCl_3$; that of stannous chloride with respect to its oxidation to stannic chloride ($SnCl_4$) is that corresponding to the formula $\frac{1}{2}SnCl_2$, and those of manganese heptoxide (Mn_2O_7) with respect to its reduction to MnO_2 and to MnO are the weights corresponding to $\frac{1}{6}Mn_2O_7$ and to $\frac{1}{10}Mn_2O_7$, respectively. The equivalent weights of elementary substances are similarly determined; thus, it follows from the formulas $AgCl$, $ZnCl_2$, and $AlCl_3$, and the combining weights of the elements (§ 16), that the equivalent weight of silver is 107.93, that of zinc, 32.70, and that of aluminum, 9.037. In cases where an element exists in two different states of oxidation, like mercury in mercurous and mercuric chloride ($HgCl$ and $HgCl_2$), or tin in stannous and stannic chloride ($SnCl_2$ and $SnCl_4$), it has two different equivalent weights with reference to its conversion into each of these states; thus the two values are 200 and 100 for mercury, and 59.50 and

29.75 for tin, since the combining weights of these elements are 200.0 and 119.0, respectively. These examples and that of manganese heptoxide just preceding them illustrate the necessity, in cases where a substance can be converted into two or more other states of oxidation, of specifying in connection with the equivalent weight what reaction is under consideration.

An important unit of concentration, which is most commonly used in connection with solutions, is also based on the definition of equivalents ; namely, when one equivalent of a substance is contained in one liter of a solution, the concentration of the substance is said to be *normal*, and, in general, concentration values are expressed by prefixing to the word normal a number equal to that of the equivalents contained in one liter. Thus, a 0.1 normal solution of sulphuric acid is one containing 4.904 grams of it in a liter of solution. Designating the number of equivalents of any one substance by n (which is equal to m / a, where m is the weight and a the equivalent weight of the substance), and designating by v the volume of the solution in which they are contained, the equivalent concentration c is defined by the relation, $c = n / v$.

20. General Significance of the Properties of Gases. — The properties of gases under moderate pressure are of so great importance, not only from the stand-point of general chemistry, but also from that of the laws of energy, that they deserve consideration among the general principles of physical science. The laws regarding the relation of their volume to pressure, temperature, and combining weight will be here discussed, while those regarding their energy-relations will be considered in the next Chapter.

21. Relation between the Pressure and Volume of Gases. Boyle's Law. — In the case of gases having pressures not greatly exceeding that of the atmosphere, the following simple relation, known from its discoverers as *Boyle's* or *Mariotte's Law*, has been found to exist between pressure and volume : *At constant temperature, the volume*

of a definite quantity of gas is inversely proportional to its pressure. Since the density of a substance is defined to be the ratio of its mass to its volume, this law may also be stated as follows : *At constant temperature, the density of a gas is directly proportional to its pressure.* Thus, if a quantity of gas occupied a volume of one liter at a pressure of one atmosphere, its volume at a pressure of two atmospheres would be half a liter ; at three atmospheres, one-third of a liter ; and so forth : and its density, or the weight of 1 ccm. of it, would be twice as great at two atmospheres, three times as great at three atmospheres, and so forth.

Boyle's Law is expressed mathematically as follows :

$$\frac{p\,v}{m} = \frac{p}{D} = \text{const.,}$$

where p, v, m, and D are the pressure, volume, mass, and density, respectively, of a definite kind of gas at a definite temperature.

The units employed for the measurement of mass and volume have been already defined, but a statement is necessary in regard to those used for the measurement of pressure. Pressure is expressed in the centimeter-gram-second system in dynes (a unit defined in § 29) per square centimeter. Another unit of pressure that is frequently employed is the *atmosphere*, which is defined to be equal to the pressure exerted by a column of mercury, 76 cm. in height, of a density of 13.59593 (which is almost exactly the value at 0°), and submitted to the *normal intensity of gravity*, which is so defined as to be almost exactly equal to the average intensity at the sea-level in the latitude of 45°. One atmosphere is approximately the mean value of the atmospheric pressure at the sea-level. It is also very common in experimental work to express pressure in terms of the height of a mercury column, reduced to the conditions just described, which exerts a pressure equal to that to be measured.

There is scarcely any doubt that Boyle's Law is also applicable to the components of a mixture of two or more

gases.   That is, *each component of a gaseous mixture exerts the same pressure as it would if it were alone present in the volume occupied by the mixture.*   The pressures exerted by the separate components are called the *partial pressures,* and this principle in regard to their values is known as *Dalton's Law.*   The law has not received direct experimental verification, owing to the difficulty of obtaining satisfactory semipermeable walls (§ 8) against which the partial pressures might be accurately measured; but its validity is made almost certain by the fact that the total pressure exerted by a gaseous mixture, which is of course the sum of the partial pressures, is found to be equal to the sum of the pressures calculated by Boyle's Law for the separate components.   In illustration of this law, the following facts may be cited. When two liters of oxygen and one liter of nitrogen, both at the pressure of one atmosphere, are mixed, and the volume of the mixture is maintained at three liters, the pressure is found to be still one atmosphere, which is in accordance with Dalton's Law; for the partial pressure of the oxygen should have become two-thirds, and that of the nitrogen, one-third of an atmosphere.   If the volume of the mixture is reduced to one liter, the pressure is found to be three atmospheres, the partial pressures of the oxygen and nitrogen having undoubtedly become two atmospheres and one atmosphere, respectively, as Dalton's Law requires.

A gas which is considered to conform completely to Boyle's Law is called a *perfect* or *ideal gas.*   No such gas actually exists, however; for Boyle's Law is not in any case absolutely exact.   In the case of gases whose temperature is far above that of liquefaction, the deviations from it are small until high pressures are reached; in the case of gases in the neighborhood of their points of liquefaction, considerable deviations exist, even at low pressures.   The following table gives an idea of the magnitude and direction of the deviations in the case of some common representative gases. The values in the columns headed $p_1v_1 : p_2v_2$ are the ratios

of the pressure-volume product at one atmosphere's pressure (p_1) to that at two atmospheres' pressure (p_2), at a temperature of 8°, unless otherwise specified. Between these pressures, the deviations will be seen to vary from about 0.05 to 2.0 per cent. in the case of the different gases. The table also contains some examples illustrating the effect of temperature on the deviations.

Name of the gas.	$p_1v_1 : p_2v_2.$	Name of the gas.		$p_1v_1 : p_2v_2.$
Hydrogen	0.9995		8°	1.0065
Nitrogen	1.0007	Carbon dioxide	50°	1.0036
Nitric oxide	1.0028		200°	1.0008
Nitrous oxide . . .	1.0065		8°	1.0209
Ammonia	1.0188	Sulphur dioxide	50°	1.0110
Cyanogen	1.0235		200°	1.0021

As the pressure continues to increase, in all cases except that of hydrogen, the values of the product pv continue to decrease, pass through a minimum, and then steadily increase; in the case of hydrogen, a regular increase takes place from the start.

Expressed in mathematical form, it is found that the behavior of hydrogen up to very high pressures is represented by the equation, $p(v-b) = $ const., and that of other gases by the so-called *van der Waals' equation,*

$$\left(p + \frac{a}{v^2}\right)(v-b) = \text{const.,}$$

in which equations a, b, and const. represent constants, which vary with the nature and quantity of the gas. For example, in the case of ethylene, a gas which deviates greatly from Boyle's Law, the values at 20° of pv calculated with the help of this last equation agree closely with those experimentally determined, even up to a pressure of 400 atmospheres, if appropriate values of the constants be assumed. This is shown by the following table, in which are given the pressures,

expressed in atmospheres, and the observed and calculated values of pv, an arbitrary unit of volume being employed.

Pressures	31.6	46	84	133	234	329	399
pv observed	0.914	0.781	0.399	0.520	0.807	1.067	1.248
pv calculated	0.895	0.782	0.392	0.520	0.805	1.067	1.254

The following figure illustrates the behavior of hydrogen and nitrogen at 60°, of carbon dioxide at two temperatures (60° and 40°), and of a perfect gas (marked P. G. in the figure), up to a pressure of 320 meters of mercury. The values of the product pv are plotted as ordinates, and the pressures (in meters of mercury) as abscissas; such quantities of the gases being taken that the initial value of pv is the same in each case.
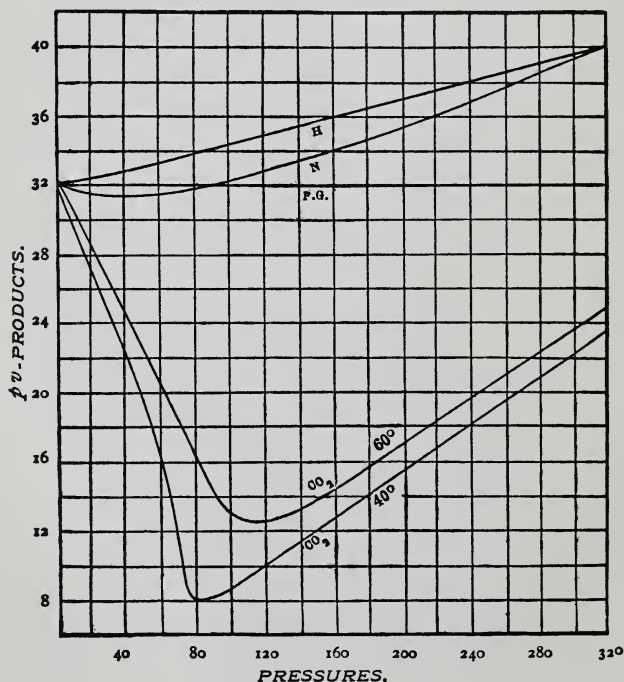
22. Relation between the Pressure-Volume Product and Temperature. Gay-Lussac's Law of Temperature-Effect. — The following principle, known as Gay-Lussac's Law of Temperature-Effect, has also been experimentally established: *A definite change of temperature causes, in the case of different gases, the same fractional change in the pressure-volume product:* if the pressure is kept constant, it causes in all gases the same fractional change in volume; and if the volume is kept constant, it causes in all gases the same fractional change in pressure.

For example, when 1000 ccm. of air at 0° are heated at the atmospheric pressure to 100°, the volume becomes 1367 ccm.; and when 500 ccm. of hydrogen are heated in the same manner, the volume becomes about 683.5 ccm.; the fractional increase (36.7 per cent.) being the same in the two cases. If a quantity of either air or hydrogen, having at 0° a pressure of one atmosphere, is heated to 100° in a vessel of constant volume, the pressure increases to 1.367 atmospheres.

It will be noted that this law states only that temperature has the same effect in the case of different gases, but does not show what the functional relation is between temperature and the pressure-volume product. This relation will, of course, depend on the scale that has been adopted for the measurement of temperature; specifications in regard to this scale must therefore be here presented. It has been agreed by physicists to adopt as the unit for the measurement of temperature the centigrade *degree*, which is defined to be the difference in temperature which produces in the pressure of a quantity of hydrogen gas one one-hundredth part of the variation in its pressure which occurs when its volume is kept constant and its temperature is changed from that of ice melting to that of water boiling under the pressure of one atmosphere. As it has been found that the fractional increase in pressure varies slightly with the initial pressure of the gas, it is necessary to specify also a definite initial pressure; accordingly, it is agreed that the

pressure of the gas at the temperature of melting ice shall
be that of one meter of mercury.   In order to express the
temperature absolutely, it is also necessary to adopt some
arbitrary zero-point; and as such, the temperature of ice
melting under a pressure of one atmosphere has been chosen.
Temperatures referred to this scale and to this zero-point
are designated *normal temperatures* (*t*).   In many theo-
retical considerations it is simpler to adopt such a zero-point
that temperatures will be directly proportional to the
pressures which they produce in a quantity of hydrogen
gas; now, since its pressure at the temperature of melting
ice is found to increase $\frac{100}{273.0}$ when the gas is heated to 100°,
this proportionality will be secured if a zero-point 273.0°
lower than the normal zero be adopted.   Temperatures
referred to this zero-point are called *absolute temperatures*
(*T*), by reason of a relation to the Second Law of Ener-
getics that will be explained in Chapter IV.   It is evident
that $T = 273.0 + t$.

Now, since the change in pressure of hydrogen gas
has been adopted as the ultimate standard for the measure-
ment of temperature, and since by the Law of Gay-Lussac
temperature has the same effect in the case of *all* gases, it
follows that *the change in the pressure-volume product of any
gas is directly proportional to its change in temperature.*
This statement, which embraces the definition of temper-
ature and the Laws of Gay-Lussac and Boyle, is mathe-
matically expressed by the equation:

$$p\,v = p_0\,v_0\,(1 + \alpha\,t),$$

where α is a quantity (known as the coefficient of expansion)
which has nearly the same value for all gases, and where
p_0, v_0, and p, v, represent the corresponding pressures and
volumes of the gas at 0° and t°, respectively.   The value of α,
which is by definition equal to the fractional increase which
the pressure-volume product undergoes when a gas is heated
from 0° to 1°, has been already stated to be $\frac{1}{273}$ in the

case of hydrogen. By substituting this value, the last equation can be transformed into the following one :

$$\frac{p\,v}{t+273} = \frac{p_0\,v_0}{273} = m \times \text{const. (for a definite gas).}$$

With the help of the concept of absolute temperature, this principle may be stated more simply as follows : *The pressure-volume product of a definite quantity of any definite gas is proportional to its absolute temperature.* It is expressed by the equation :

$$\frac{p\,v}{T} = m \times \text{const.,}$$

in which the constant is evidently the value of the ratio $p\,v\,/\,T$ for 1 gram of any definite gas. Its value is different for different gases, however.

Attention may also be called to the fact, which is sometimes overlooked, that, though the *absolute* increase in the pressure or volume of a definite quantity of a gas is the same for 1°, whatever may be the temperature, the *relative* or *fractional* increase is variable, being always one Tth part of the initial value. For example, a gas increases $\frac{1}{273}$ of its volume measured at 0° whether it is heated at constant pressure from 0° to 1° or from 100° to 101°; but in either case it increases not $\frac{1}{273}$, but $\frac{1}{373}$, of its volume measured at 100°. The ratio $p\,v\,/\,T$ is evidently the absolute increase in the product $p\,v$ due to an increase of temperature of 1° at any temperature T.

The Law of Gay-Lussac, like that of Boyle, is not absolutely exact ; that is, equal changes in temperature do not produce in all gases *exactly* the same change in the product $p\,v$. This is shown by the following table, which contains the values of the fractional increase in pressure (100 $\propto$) which different gases undergo when they are heated from 0° to 100°, the volume being kept constant and the initial pressure being that of one meter of mercury.

Name of the gas.	100α.	Name of the gas.	100α.
Hydrogen	0.3662	Carbon dioxide . . .	0.3725
Nitrogen	0.3675	Sulphur dioxide . . .	0.3845
Carbon monoxide . .	0.3667		

It will be seen that all the very difficultly liquefiable gases (those contained in the first column) have nearly the same values, while the more easily liquefiable gases (those contained in the second column) have considerably larger values.

23. Relation between the Pressure-Volume Product and Combining Weight. Gay-Lussac's Law of Combining Volumes. — In addition to the laws already considered, an important relation between the pressure-volume product for substances in the gaseous condition and their combining weights has been established by experiment. This relation may be stated as follows: *The combining weights of all substances in the gaseous condition have at the same temperature equal values of the pressure-volume product, or values of it which stand to one another in the ratio of small whole numbers.* If the volume occupied by the combining weight of a substance is called its *combining volume,* the law may also be stated thus: *The combining volumes, measured at the same temperature and pressure, of all substances in the gaseous condition are equal, or stand to one another in the ratio of small whole numbers.* This law is called the *Gay-Lussac's Law of Combining Volumes.*

. For example, two volumes of hydrogen unite with one volume of oxygen to form water; one volume of ammonia unites with one volume of hydrochloric acid gas to form ammonium chloride; two volumes of benzene-vapor require fifteen volumes of oxygen for their complete combustion, and twelve volumes of carbon dioxide and six volumes of water-vapor are formed as products. To substances which are not together involved in any one definite chemical reaction the principle is also applicable; for their combining

weights can always be determined indirectly, by comparisons of their elementary compositions or of the quantities of them involved in reactions with other substances. Thus, the combining weights of ammonia and hydrogen, determined, for example, by comparing the quantities of them combined with a definite quantity of chlorine in the compounds ammonium chloride and hydrochloric acid, are to each other as 17.06 : 1.008, and the combining volumes of these substances, that is, the volumes of 17.06 grams of ammonia and of 1.008 grams of hydrogen, are to each other as 2 : 1.

Gay-Lussac's Law of Combining Volumes is subject to deviations of the same order of magnitude as those which affect the validity of the Boyle's Law and Gay-Lussac's Law of Temperature-Effect. For example, the volumes of hydrogen and oxygen, measured at 0° and 76 cm. pressure, which combine with each other to form water are not as 2 : 1, but, according to the accurate experiments of Scott and Morley, as 2.0027 : 1. In the case of readily liquefiable gases, the deviations from whole numbers are much greater.

24. General Expression of the Pressure-Volume Relations of Gases. Empirical Definition of Molecular Weight. — It was mentioned above that the product pv / T has a different value for equal weights of different gases; thus, when absolute units are employed, it has the value of 2 600 000 for 1 gram of oxygen, and the value 41 200 000 for 1 gram of hydrogen. Since, however, its value for different weights of a definite gas is proportional to those weights, it is evident that the relative weights of different gases which have the same value of the product pv / T can be readily calculated, and that these weights can be expressed absolutely by adopting a definite weight of some definite gas as a standard of reference. It has been agreed to adopt 32 grams of oxygen as the standard, and to designate that quantity of any other gas that has the same value of the product pv / T as 32 grams of oxygen, the *molecular weight*, or *one mol*, of the gas.

In consequence of the Law of Combining Volumes and the adoption of twice the combining weight of oxygen as the standard, it is evident that the molecular weight of any sub-stance is equal to its combining weight, or stands to it in the relation of some small whole number. But since the Law of Combining Volumes is not exact, and since as a rule gaseous densities are not determined with as great accuracy as the combining weights, the following, exact definition, based both on combining weights and on the volume-relations of gases, has been adopted : the *molecular weight* or *one mol* of any gaseous substance is that small multiple or sub-multiple of its combining weight which has approximately the same value of the product $p\,v\,/\,T$ as 32 grams of oxygen.

While the name molecular weight originated from cer-tain hypothetical considerations connected with the quantities denoted by it, it is clear that these quantities as here defined are experimentally determinable ones, and are not based on any hypothesis whatever.

With the help of this definition of molecular weight, the volume-relations of gases under moderate pressures can be fully expressed by the following highly important, general equation :

$$p\,v = N\,R\,T$$

in which p, v, and T signify, as usual, the pressure, volume, and absolute temperature of the gas ; N is the number of mols present in it, and is evidently equal to $m\,/\,M$, where m is the weight, and M the molecular weight, of the gas ; and R is a constant for all gases, equal to the value of $p\,v\,/\,T$ for one mol of any gas.

The numerical value of the constant R is readily calcu-lated from the data pertaining to oxygen : according to the exact determinations of Morley, one gram of this gas under the so-called *normal conditions*, that is, at 0° and a pressure of one atmosphere, occupies a volume of 699.8, or almost exactly 700 ccm., so that 32 grams of it occupy a volume of 22 400 ccm. or **22.4** liters, a value which (like all others that

in this book are represented by bold type) it is well to remember, since it is the volume of one mol of any gas under normal conditions. Therefore,

$$R = \frac{p\,v}{NT} = \frac{1 \times 22.40}{1 \times 273.0} = 0.0820,$$

when the pressure is expressed in atmospheres and the volume in liters. If the pressure is expressed in dynes and the volume in cubic centimeters, $R = 8.31 \times 10^7$.

It is evident, if four of the five factors (m, M, p, v, T) on which depend the volume properties of gases, are known, that the remaining one can readily be calculated by this equation. As in all numerical applications of algebraic expressions, care must be taken that the units in which the corresponding quantities (here the constant R and the five variables) are expressed, be identical.

By dividing both members of the equation $p\,v = NRT$ by m, the weight of the gas, and substituting for $m\,/\,v$ the density D, and for $m\,/\,N$ the molecular weight M of the gas, the equation, $M = DRT\,/\,p$, is obtained. This states that, at constant temperature and pressure, the molecular weights of gases are proportional to their (absolute) densities. Since the molecular weight of oxygen $M_O = 32$, the molecular weight of any gas is equal to **32** times the ratio of its density to that (D_O) of oxygen at the same temperature and pressure; that is, $M = 32\,D\,/\,D_O$. Since experimentally determined densities are often referred to the density of air (D_A) instead of that of oxygen, it is worthy of note that $D_A : D_O :: 28.97 : 32$, or very nearly as **29 : 32.**

It is customary to employ for gaseous substances whose densities have been determined, chemical formulas corresponding to that multiple of the combining weight, which is the molecular weight as above defined. Such formulas are called *molecular formulas.* They evidently express not only the nature and relative quantities of the component elements, but also the value of the pressure-volume product for any weight of the gaseous substance. The formula-

weight of a gaseous substance thus becomes identical with its molecular weight. It is also the practice, when reasons for another procedure do not exist, to represent the liquid and solid substances into which gaseous substances are converted by withdrawal of heat, by the same molecular formulas, and to designate the weights corresponding to these formulas as one mol of the substances.

For example, liquid benzene is found by analysis to contain 92.25 per cent. of carbon and 7.75 per cent. of hydrogen. By dividing these percentages by the combining weights of the elements (12.00 and 1.008, respectively), it is found that the substance contains an equal number of combining weights of the two elements. Its combining weight is therefore 13.01 and its empirical formula is CH. Its density, when in the form of vapor at 100°, has been determined and found to be 2.47 times as great as that of oxygen at that temperature when under the same pressure. The molecular weight of it is therefore approximately $32 \times 2.47 = 79.0$, which is nearly six times the combining weight deduced from the analysis. The exact molecular weight is therefore 78.06, and the molecular formula is C_6H_6.

It is frequently desirable to express the concentration of a substance in terms of the number of mols per unit of volume ; and it has recently been proposed to use the adjective *molar* to signify one mol per liter, and to prefix to this word numbers to indicate fractions and multiples of one mol per liter. Thus, a 0.05 molar solution of benzene in alcohol is one which contains $\frac{1}{20}$ mol or 3.903 grams of benzene in one liter of the solution. In general, designating by N the number of mols of any one substance contained in the volume v, the molar concentration C is expressed by the relation, $C = N/v$. The general adoption of this term molar seems highly desirable, in order to avoid the serious confusion which is beginning to arise through the use of the term normal by some writers in the sense of one mol, as well as in its appropriate sense of one equivalent, per liter.

CHAPTER IV.

THE GENERAL PRINCIPLES RELATING TO ENERGY.

25. The Forms of Energy and Other Classes of Energy Manifestations. — Energy has been already defined (§ 6) to be that which gives rise to the changes in the properties of bodies and to the power which bodies, or in some cases portions of unoccupied space, possess of producing such changes. It has also been stated that the manifestations of energy are most varied in character. Nevertheless, it has been found possible to refer all of them to a comparatively small number of so-called *forms of energy*, each form corresponding to a certain definite tendency in the body possessing it to undergo a change in position or condition. The forms of energy which may be associated with matter are designated as follows:

1. *Kinetic Energy.*   5. *Electrical Energy.*
2. *Gravitation Energy.*   6. *Magnetic Energy.*
3. *Cohesion Energy.*   7. *Chemical Energy.*
4. *Disgregation Energy.* 8. *Heat Energy.*

Kinetic energy is the energy that bodies possess in virtue of their motion. *Gravitation energy* is the energy that bodies possess in virtue of their inherent tendency to approach one another. *Cohesion energy and disgregation energy* are terms here employed to designate the forms of energy a body possesses in virtue of the tendency of its particles to approach one another, and to recede from one another, respectively. The existence of cohesion energy is shown by the contraction of solid and liquid bodies upon cooling, by the tendency of a stretched piece of wire or rubber to become shorter, by the attraction of two carefully ground plates laid close together, and by the tendency of the surface of liquids to diminish in extent, as is illustrated

by drops of water assuming a spherical form and by capillary phenomena, such as the rise of liquids in narrow tubes. Disgregation energy is exhibited by all gases and by compressed liquids and solids; for these have the power of producing changes in virtue of the tendency of their particles to separate. *Electrical and magnetic energies* cannot be intelligibly defined in a few words; it is sufficient at this point to state that they are the forms of energy corresponding to those properties of bodies which are treated of in the divisions of physics known as Electricity and Magnetism. *Chemical energy* is the energy that bodies possess in virtue of the tendency of the chemical substances present in them to undergo transformations into other substances. *Heat energy* is the energy that bodies possess in virtue of the tendency of their temperatures to decrease: it is the energy which is given out by bodies when they are brought into communication with surroundings of lower temperature.

Energy manifestations may also be considered from other points of view. A convenient classification of some of them, based on the space relations of bodies, may be here mentioned. The energy which bodies possess in virtue of their tendency to approach or recede from one another is called *distance energy*, without reference to the *form* of energy, as above defined, from which the tendency may arise; thus, gravitation energy is by nature a form of distance energy, but electrical and magnetic energies also give rise to it under certain conditions, as is illustrated by the attraction and repulsion which electrically charged bodies or magnetized bodies exert on one another. The powers of doing work (a term defined just below) which bodies possess in virtue of their tendencies to undergo changes in surface, volume, and form, are called *surface energy, volume energy,* and *elastic energy,* respectively. These are special manifestations of cohesion and disgregation energies rather than distinct forms of energy. Surface energy is of especial importance in the case of liquid bodies, whose

surfaces always tend to diminish in extent, as was illustrated above. Volume energy is exhibited by all compressed bodies, whether solid, liquid, or gaseous. Elastic energy, as distinct from volume energy, is possessed only by solid bodies : it is the energy that is developed in them by the external application of pressure or tension, and it is the resultant of the changes thereby produced in the cohesion and disgregation energies within the bodies. Thus, the elastic energy of a bent steel spring or a stretched wire is due both to the cohesion energy of the extended parts and to the disgregation energy of the compressed parts of the spring or wire. In the interpretation of most phenomena the consideration of the surface, volume, and elastic energies has a great advantage over the consideration of the cohesion and disgregation energies involved, since the former are determined by their external manifestations and are therefore capable of quantitative measurement (as is described in § 30), while, as a rule, the latter are not accessible to it.

The general term *potential energy* is used to designate the energy that bodies possess in virtue of their position or their configuration : it includes the four classes of energy-manifestations considered in the preceding paragraph. The term *mechanical energy* includes kinetic energy in addition to these.

A convenient term in common use, closely related to energy, is the term *work*, which is used to designate the quantities of all forms of energy except heat, involved in any process of energy transformation or transference ; it therefore signifies the quantities of the various forms of mechanical energy, of electrical and magnetic energies, and of chemical energy, that undergo change in form or location in any process. Thus, it is customary to speak of the transformation of heat into work, for example, by the steam engine when it produces motion or electrical energy, raises a weight, compresses a gas, etc., and in general of the production of both heat and work in the surroundings when

a body parts with a portion of its energy, the two terms heat and work being considered to embrace all forms of energy produced. The work is said to be done *by* the body which parts with its energy *upon* the body whose energy is increased. Thus, work is done by an explosive at the expense of its chemical energy on the cannon ball which it sets in motion, and by the steam engine at the expense of the heat energy of the steam upon the body which it raises. The reason for thus distinguishing heat from other forms is the existence of the Second Law of Energetics, which is discussed below. It should be added that in the science of Mechanics the term work is used in a more specific sense, namely, to designate the energy-change corresponding to the displacement of a force through a distance; in this book, however, it will be used only in its general sense.

The rate at which energy is transferred from one body to another, or transformed from one form to another, is called *activity*, or in engineering practice, *power*, when the transference or transformation is of such a character that work is said to be done. That is, activity or power is the ratio $(dW / d\tau)$ of the work done (dW) to the time $(d\tau)$ in which it is done.

Although there are no phenomena that furnish direct manifestations of energy unaccompanied by the manifestations of matter (§ 7), yet there are phenomena which justify the inference that energy does exist unassociated with matter. Thus, this inference is to be drawn from the fact that portions of space which contain no matter, under some conditions possess the power of producing changes in the properties of bodies that are introduced into the space. In illustration of this statement, the following phenomena may be cited: any non-transparent body, even if surrounded by a vacuum, when placed in a sunbeam acquires the property of visibility; a thermometer with blackened bulb similarly placed indicates by the extension of its mercury column a rise of temperature; and in a metal ring

interrupted by a small spark-gap electric sparks are produced when it is suitably placed near a circuit having a spark-gap across which electric discharges are taking place. In addition to the forms of energy associated with matter, which have been already considered, it is therefore necessary to recognize another form in which energy exists unassociated with matter. This form, which is known as *radiant energy*, may be defined as the form in which energy is transmitted from one body to another through space without the mediation of ordinary matter. Various manifestations of it may be distinguished : the most important are *light, radiant heat,* and *electromagnetic radiations*, which are capable of producing in bodies the properties of visibility, increased temperature, and electrification or magnetization, respectively. They are illustrated by the three examples just cited. Besides these, there have been recently discovered other more special varieties of radiant energy, such, for example, as are possessed by the so-called Röntgen Rays and Becquerel Rays.

    * The general definition of energy, given above, as that which gives rise to the changes in properties of bodies, is not that which is customary in treatises on physics, where it is usually defined as the power of doing work. The latter definition is open, however, to the objection that it presupposes a definition of work, which cannot, of course, in this case logically be defined in terms of energy, as has been done above, but must, therefore, be defined in terms of some less fundamental concept, that of force being usually employed. Another definition, which has recently been proposed, is, energy is the power to change the state of motion of a body. While the same objection does not apply to this, both these special definitions have the disadvantage of giving undue prominence to one particular form of energy, and tend towards an exclusively mechanical interpretation of natural phenomena. Another, more serious objection to these definitions is the fact that the essence of one of the fundamental laws relating to energy — the

so-called Second Law of Energetics — is that heat energy and the power of doing work actually are not equivalent, but are sharply differentiated. The usual definition is therefore a source of confusion. The general definition given at the beginning of this section, though it furnishes a sufficient criterion for detecting the presence of energy in any body or space, is, to be sure, not definite enough to form a basis for the quantitative measurement of energy; further specifications in regard to the latter are therefore necessary.

26. **The Quantitative Measurement of Energy.** — In order to measure quantities of energy of different forms, it is necessary to convert them into the same form, and compare the quantities of it so produced with some standard quantity of it adopted arbitrarily as a unit. Since gravitation and kinetic energies, unlike the other forms, can be fully expressed in terms of matter and space, or matter, space, and time, without the introduction of any new concept, it is simplest in principle to adopt a unit-quantity of one of these forms for the expression of quantities of energy in general; moreover, the pre-eminent technical importance of mechanical energy furnishes additional reason for the adoption of some form of it as a standard of reference. Some unit of energy based upon mechanical relations has therefore been universally adopted as the fundamental one.

The centimeter-gram-second unit of energy is called the *erg*. It is most simply defined as that amount of energy which is equal to twice the kinetic energy possessed by a mass of one gram when moving with a velocity of one centimeter per second. As this unit is a very small quantity, a unit ten million times greater, called the *joule*, is often employed; that is, 1 joule $= 10^7$ ergs. The reason for the apparently irrational definition of the erg as *twice* the stated quantity of kinetic energy is a historical one, and will be explained in § 29.

Units of heat energy are, however, also extensively employed, especially by reason of the fact that other forms of

energy are readily and completely transformed into heat, so that it is the form which is in general best adapted for the experimental determination of quantities of energy. The unit of heat will be here defined as the quantity of heat required to raise the temperature of 1 gram of water from 17° to 18°. This unit is called the *calorie at 17.5° (cal.)*, and it is the one that will be always used in this book. It is to be noted, however, that usage unfortunately varies with respect to the temperature adopted in the definition, and that, therefore, the calorie used by different scientists varies somewhat in value (decreasing by 0.03 per cent per degree between 15° and 25°). Moreover, certain other heat units are in common use. Of these will be here mentioned only the *mean calorie*, which is one one-hundredth part of the heat required to raise the temperature of 1 gram of water from 0° to 100°. According to recent determinations, the mean calorie differs from the calorie at 17.5° by less than 0.1 per cent.

The relation between the mechanical and thermal units is evidently of very great importance, and it has been determined with great care by several experimenters. The number of units of mechanical energy which correspond to one unit of heat energy is called the *mechanical equivalent of heat* (J). Its value in the centimeter-gram-second system has been found experimentally to be 41 840 000. That is, 1 calorie $= 4.184 \times 10^7$ ergs $= 4.184$ joules, or approximately **4.2** joules.

It should be added that it is now becoming a common practice to express quantities of heat in joules instead of calories, the direct results of calorimetric measurements being reduced to the mechanical unit with the help of the mechanical equivalent of heat.

The unit of activity or power in the centimeter-gram-second system is that involved when one erg of work is done per second. No name has been given to this; for a unit ten million times as large is far more commonly employed. This

latter unit is called the *watt,* and is the rate at which work is done when one joule of energy is transferred or transformed per second.

27.   **The Law of the Conservation of Energy, or the First Law of Energetics.** — The essential idea involved in the concept of energy and throughout the above considerations relating to it is the *constancy* of a quantity which is involved in all the changes taking place in the universe; and this is often explicitly expressed by the statement that *energy is neither created nor destroyed in any process whatever.* This statement is called the *Law of the Conservation of Energy* or the *First Law of Energetics,* the name *Energetics* being applied to that branch of science which treats of the general principles relating to energy. This law may also be stated more concretely as follows: *When a quantity of energy disappears at any place, a precisely equal quantity of energy simultaneously appears at some other place or places, and when a quantity of energy disappears in any form, a precisely equal quantity of energy simultaneously appears in some other form or forms;* equal quantities of energy of different forms being understood to be such quantities as produce the same effect (for example, in modifying motion or raising temperature) when converted into the same form.

This law is to be regarded as one of the most certain, as well as one of the most fundamental, laws of science. The exactness of it has been established by a considerable number of careful quantitative investigations made for the purpose. Thus, the various determinations of the mechanical equivalent of heat have proved that a definite quantity of mechanical energy, such as that possessed by a raised weight, when transformed into heat, always gives rise to a definite quantity of heat, whatever may be the process used for the transformation ; for example, in one method a weight while gradually falling kept a paddle-wheel in motion which by its friction against the water of a calorimeter produced the heat, while

in another method a weight was allowed to fall freely and to strike upon a mass of lead, which became heated as a result of its compression. Such determinations have also shown that those quantities of electrical energy, kinetic energy, gravitation energy, and volume energy (of compressed gases) which are transformable into one another produce equal quantities of heat, thus proving that there is no change in the total energy when these four forms are converted into one another. The law is also confirmed by the correspondence of the conclusions drawn from it with well-established facts and principles. Among these may be mentioned as most important the following principle, which is a conclusion based upon the failure of innumerable attempts to produce a contrary result : *The production of an unlimited amount of work by a machine or arrangement of matter which receives no energy from the surroundings is an impossibility.* An ideal process like that here stated to be impossible of realization is sometimes called *perpetual motion of the first kind.*

It is often desirable in applications of the Laws of Energetics to differentiate the energy-changes occurring within a definite body or group of bodies, that is, within the *system* under consideration, from the related changes which may simultaneously occur in the *surroundings*, and to differentiate further the energy-changes in the surroundings into work and heat-changes, as described in § 25. Thus, the total energy within a definite system (not including, however, its kinetic energy) is commonly called its *internal energy* (U); and the requirement of the First Law that the difference ($U_2 - U_1$) in its values after and before any change be equal to the quantity of heat (Q) absorbed from the surroundings diminished by the work (W) done by the system on the surroundings (called the *external work*), is expressed by the equation :

$$U_2 - U_1 = Q - W.$$

It is to be noted that here and always in this book Q repre-

sents the heat *absorbed by the system*, and W the work *pro-duced in the surroundings*, and therefore that the numerical value of Q is positive when heat is actually absorbed and negative when it is evolved, and that that of W is positive when work is done by the system upon the surroundings and negative when done by the surroundings upon the system.

The value of the increase in the internal energy is evidently equal to the heat absorbed by the system when the same change in state takes place under such conditions that no external work is done; that is, $U_2 - U_1 = Q$, when $W = 0$; and it is commonly so determined.

Consider as an example the change consisting in the volatilization at 100° of 1 gram of liquid water (whose volume is 1.043 ccm.) to form vapor (volume, 1661 ccm.) against the constant pressure of one atmosphere. Since the heat absorbed by the system during the change (the ordinary heat of vaporization) is 537 cal., and the work done as the result of the expansion can be calculated (see § 30) to be 168 joules, the values in the above equation become:

$$U_2 - U_1 = (537 \times 4.184) - 168 = 2082 \text{ joules.}$$

This last value, the increase in the energy of the water as a result of its vaporization, is equal to the heat that would be absorbed if the water were vaporized within a vessel of constant volume; for then no external work would be done.

Another example of quite a different kind is that of a chemical change which is accompanied by the production of electrical energy. Consider a system consisting of a silver plate immersed in a silver nitrate solution and a copper plate in a copper nitrate solution, the two solutions being in contact with each other, and the two plates being connected with wires by which the electrical energy produced is transferred to the surroundings; consider further that the chemical change takes place which is expressed quantitatively as well as qualitatively by the equation:

$$Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag.$$
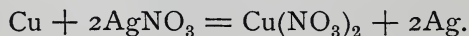
Since this change is known to evolve 8920 cal. when taking place under the stated conditions (that is, so that electrical energy is produced), and to evolve 30040 cal. when no external work is done (for example, when the plate of copper is placed directly in the silver nitrate solution), the equation, $U_2 - U_1 = Q - W$, becomes, $(-30040) = (-8920) - E_E$, or $E_E = 21120$ cal., where E_E represents the electrical energy produced.

28. The Factors of Energy in General.— Experience shows that whether or not a transfer of any form of energy from one place to another takes place, and in which direction it takes place, is not determined by differences in the *quantities* of the energy in the two places. It is therefore necessary to ascribe to every form of energy a characteristic property which gives rise to this phenomenon of transference. This property is called the *intensity* of the energy, and is assumed to have a greater value at the place where the quantity of energy diminishes, and a smaller one at the place where it increases. Therefore, wherever a transference of energy takes place, a *difference of intensity* must exist.

For example, when a small vessel of water is placed within a larger one, it often happens that no transfer of heat takes place, although the amount of heat contained in the larger vessel may be much greater; while in other cases it will be found that heat passes from the smaller to the larger vessel, or the reverse, making it evident that it is not the quantity of heat, but some property of it, that determines its transference; this property is in this case the familiar one called *temperature*. Similarly, if two reservoirs of gas are connected with the opposite ends of a closed cylinder containing a movable piston, it is found that whether or not motion of the piston takes place, or in which direction it takes place, does not depend on the quantities or the volumes of the two gases, or on the quantities of energy contained in them, but on the particular property which is

called *pressure.* Temperature and pressure are, then, the intensities of heat and volume energies, respectively.

It is always found that, other things being equal, the quantity of energy involved in any transference of energy is greater, the greater the difference in intensity. Therefore, if an arbitrary scale, such as has been already described in the case of temperature, be adopted for the measurement of intensity-differences, a quantity of energy of whatsoever form may be regarded as the product of two numerical factors : one of these is the value of the intensity-difference, and the other is the quantity by which this must be multiplied in order that the product may equal the quantity of energy. This latter factor is called the *capacity-factor* of the energy. Its numerical value will evidently be equal to the quantity of energy transferred when the intensity-difference is constant and equal to unity.

Although this method of determining the factors of energy is, abstractly considered, the rational one, the reverse method is often followed, for the reason that the capacity-factor of some forms of energy is more familiar and more directly measurable than the intensity-factor. The method actually employed is therefore the following one. It is almost always possible to detect at once some one definite well-known property on which the magnitude of the energy in question depends ; for example, the energy of a moving body is obviously dependent on its rate of motion or velocity, that of a suspended body on its distance above the earth's surface, that of a hot body on its temperature. A method of quantitative measurement of this property is agreed upon, and the property is adopted as one of the factors of the energy. The other factor is thereby determined ; for it is, by definition, that quantity which when multiplied with the value of the factor already adopted will produce the energy. It is generally found that one of the two factors is the intensity of the energy, or that property of it which determines its transference. If such did not

prove to be the case, another method of resolution into factors would be attempted. Examples of two possible methods of resolution into factors are given below in the cases of kinetic and gravitation energies.

These considerations are made clearer and more definite by the following mathematical expression of them. In accordance with the preceding statements, the relation between the quantity (E) of any form of energy and the values (i and c) of its intensity and capacity factors is expressed by the equation:

$$E = i\,c.$$

That is, the value of either factor is the ratio of the value of the energy to the corresponding value of its other factor.

The differential form of this equation,

$$dE = d\,(i\,c) = i\,dc + c\,di,$$

is, however, of more general applicability; for in most cases it is not possible to measure the absolute quantity of a form of energy present in a system, although changes in its quantity may be readily accessible to measurement. It follows from this equation that:

$dE = i\,dc$, when i is constant; and
$dE = c\,di$, when c is constant.

These two equations are applied in three different ways in determining the relation between a form of energy and its factors. When the energy-change of the form in question is capable of direct measurement, some principle is adopted *either* for the measurement of the absolute value of one of the factors (i or c), whereby the change in the value of the other factor (dc or di) becomes determined, *or* for that of the value of the change in one factor (dc or di), whereby the absolute value of the other factor becomes determined; or *thirdly*, when the energy-change is not directly measurable (owing perhaps to its being necessarily accompanied by a change in some other form of energy than that in question), principles are adopted for the measurement both

of the absolute value of one factor and of the change in value of the other factor.

Numerous applications of these principles are presented in the following sections, in which the factors of the various forms of energy are considered.

29. The Factors of Kinetic and Gravitation Energies. Definitions of Force. — The kinetic energy of a body is obviously dependent on its velocity (u). Measurements of the quantities of energy possessed by the same body when moving at different velocities (made, for example, by determining the rises of temperature produced in a definite quantity of water when the motion is destroyed by friction) show, however, that these quantities are not proportional directly to the velocity, but to its square ; the *velocity-square* is therefore one of the factors of kinetic energy. Kinetic energy does not depend upon this alone, however ; for different bodies moving with the same velocity are found to have different amounts of energy ; this other factor upon which the magnitude of the energy depends, is called *mass* (m), as already stated in § 7. Finally, it is to be noted that the definition adopted for the unit of energy, the erg, causes the introduction of the coefficient $\frac{1}{2}$ into the relation between kinetic energy (E_K) and its factors. These principles and definitions are expressed in the equation :

$$E_K = \tfrac{1}{2}\, m\, u^2.$$

It is to be noted that velocity is a quantity which requires for its complete definition not only the specification of a magnitude, but also that of a direction, which last is usually expressed with reference to arbitrary co-ordinate axes, and in such a manner that velocities in opposite directions are represented by opposite signs. In the case of velocity-square, however, and therefore in that of kinetic energy, the factor expressing the direction is eliminated (since the sign of a square is positive, whatever be the sign of the quantity). Now, since bodies change their relative

positions when they possess velocities differing either in magnitude or direction, it is evident that velocity, and not velocity-square, is to be regarded as the intensity-factor of kinetic energy. Its capacity-factor then becomes the product of the mass into the velocity ($m u$), which product is commonly called *momentum*. This method of resolution is expressed by the equation, $E_K = \frac{1}{2}(m u) u$. These considerations illustrate the fact that the more obvious method of resolving an energy-quantity (that first presented in this case) may not yield a factor which has the characteristics of an intensity-factor. They also illustrate the application of the general equation, $E = i c$, to the determination of the relation of a form of energy to its factors, it being known in this case that i is equal to u, for the measurement of which units were described in § 5, and that $E = \frac{1}{2} m u^2$, whereby c becomes determined.

The most obvious and simple factor on which the quantity of gravitation energy depends, is the distance between the bodies possessing it. Newton's Law of Gravitation, when expressed in terms of energy instead of force, shows, however, that the gravitation energy (E_G) possessed by two bodies is not directly proportional to the distance (l) between them, but that it varies with the distance in the way expressed by the following equations :

$$dE_G = m'_1 m'_2 d \left(-\frac{1}{l} \right) = \frac{m'_1 m'_2}{l^2} dl,$$

$$E_{G_2} - E_{G_1} = m'_1 m'_2 \left(\frac{1}{l_1} - \frac{1}{l_2} \right),$$

where m'_1 and m'_2 are constants depending solely on the two bodies ; and where E_{G_1} and E_{G_2} are the quantities of gravitation energy possessed by them when at the distances l_1 and l_2, respectively. It is evident now that, if the function of the distance $\left(-\frac{1}{l} \right)$ were adopted as one factor of the energy, the product of the quantities m'_1 and m'_2 would be the other factor. These quantities are a permanent property of the

individual bodies, entirely independent of their variable properties, and also of the distance between them ; it is this property which was called in § 7 the capacity of bodies for gravitation energy.   By Newton's Law of Gravitation these quantities m'_1 and m'_2 are, as stated in § 7, strictly proportional to the masses m_1 and m_2 of the bodies ; that is, $m'_1 m'_2 = j m_1 m_2$, where j is the so-called gravitation-constant.

This method of resolution of gravitation energy into factors is of importance in its relation to the concept of matter ; for it shows very clearly that the property expressed by the quantities m'_1 and m'_2 derived from a consideration of the gravitation energy of bodies is just as fundamental a one as that of mass, which is derived by an entirely similar consideration of their kinetic energy.   From the energy point of view this method of resolution is not satisfactory, however ; for neither of the factors has the character of an intensity, since neither the distance between the bodies, nor any inherent property of the bodies themselves, *alone* determines the degree of their tendency to approach one another, which is found to be dependent *both* on the bodies themselves and the distance between them.   It is found, however, that, if the distance itself, instead of any function of it, is adopted as one of the factors of the energy, then the quantity by which this must be multiplied to produce the energy does have the characteristics of an intensity-factor.   This quantity is called *force*, — a term, however, which is not only used to designate the intensity-factor of the gravitation energy possessed by two bodies, but is also employed, in a manner to be now described, in a much more general sense and with reference to other forms of distance energy.

Whenever in displacing a body through a distance (dl) in any direction, an increase in its distance energy (dE_l) takes place (whereby, of course, an equivalent quantity of work must be done upon it), a *force* (F) is said to be acting

upon the body in the opposite direction, and its magnitude is defined to be equal to the ratio of the change in distance energy to the change in distance; that is, $F = dE_l / dl$. A negative value of dE_l, that is, an energy-decrease, signifies a force acting in the direction of the body's displacement.

Employing this concept of force, changes in distance energy are expressed in a most general manner by the equations:

$$dE_l = F\,dl, \text{ and } E_{l_2} - E_{l_1} = \int_{l_1}^{l_2} F\,dl,$$

The last equation becomes, $E_{l_2} - E_{l_1} = F\,(l_2 - l_1)$, when the force is constant throughout the distance traversed.

This method of resolving distance energy into factors and of defining force is evidently an application of the general equation, $i = dE / dc$, to a case where the quantities dE and dc have been first independently defined.

It follows from this definition of force and the inductively established laws of gravitation, which, as above stated, are expressed by the equations:

$$dE_G = m'_1 m'_2\, d\!\left(-\frac{1}{l}\right) = \frac{m'_1 m'_2}{l^2}\,dl = j\,\frac{m_1 m_2}{l^2}\,dl,$$

that for the force of gravitation, F_G, the following relation holds true:

$$F_G = \frac{m'_1 m'_2}{l^2} = j\,\frac{m_1 m_2}{l^2},$$

where j is the gravitation-constant. This last equation is evidently the mathematical expression of the laws of gravitation in the form in which they were stated by Newton.

Since distance energy is completely transformed into kinetic energy with great readiness, as in the case of a body falling towards the earth, a secondary definition of force can be based on the relation between these two forms of energy. This is derived immediately from the Law of the Conservation of Energy, which requires that a decrease in the

quantity of the one form of energy be accompanied by an equal increase in the quantity of the other form, provided, of course, no third form of energy is produced; that is :

$$F\,dl = d\left(\tfrac{1}{2}\,m\,u^2\right) = m\,u\,du,$$

where F represents a force which, in acting upon a body of mass m moving with a velocity u, in the direction of its motion for the time $d\tau$, during which it traverses the distance dl, produces an increase in its velocity du. From this equation it follows, since $u = dl\,/\,d\tau$ and $a = du\,/\,d\tau$ (§ 5), that

$$F = m\,\frac{du}{d\tau} = m\,a\,;$$

that is, force is measured by the product of the mass of a body into the acceleration which the force produces in its motion.

This last definition is the one originally adopted for force before the development of the doctrine of energy, and it is still retained as a primary one in most works on physics, energy being subsequently defined as the power of doing work, which in turn is defined in terms of force and distance. This procedure is liable to lead to a confusion of the fundamental with the derived concept; and it is therefore necessary to emphasize the relation and distinction between energy and force. Energy is the ultimate cause which produces the tendency in bodies to approach or recede from one another, just as it produces the tendency to all other changes; force is the characteristic which energy manifests when it tends to cause bodies to approach or recede from one another. Energy is an indestructible quantity; force is a changeable quality of energy, sometimes exhibited by it and sometimes not.

In accordance with the last equation, the value of the force F_G acting between the earth and a body of mass m, which force is called the *force of gravity*, is given by the equation, $F_G = mg$, in which g represents the acceleration of its motion which the body experiences when falling

towards the earth uninfluenced by any other cause than the force of gravity itself. The value of g is independent of the mass of the falling body, but varies somewhat with its position.

The fundamental unit employed for the measurement of force is called the *dyne;* it is the force which is acting continuously upon a body when an increase or decrease of one erg in its distance energy takes place for each centimeter of distance traversed; or, in accordance with the secondary definition of force, it is the force which when exerted on a mass of one gram for one second causes its velocity to be increased by the amount of one centimeter per second. Since the increase of velocity that takes place each second in the downward motion of a freely falling body at any place is g centimeters per second, the dyne is evidently one g-th part of the force with which, at that place, a mass of one gram tends to approach the earth. This last force is known as a force of *one gram* in the so-called Gravitational System of Units. For exact scientific purposes this system is an unsatisfactory one, since the value of the unit of force is different at different places upon the earth; it will therefore not be employed in this book. It is important to note, however, that the value of a force expressed in grams at any place is converted into the value of it in dynes by multiplying by the value of g at that place ; also, that the value of g at the sea-level in a latitude of 45° is 980.7, or approximately **980**, using as units the centimeter and second, and that variations of altitude not exceeding 3000 meters and of latitude not exceeding 10° affect this value by less than 0.1 per cent.

The definition of the unit of energy, the erg, was originally based on that of the unit of force, the dyne ; the latter having been first defined in accordance with the equation, $F = m\,a$, and the former then becoming determined by the equation, $dE = F\,dl$. This method of definition makes the kinetic energy expressed in ergs equal to *one-half*

the value of the product mu^2, as is shown by the series of relations:

$$dE_K = F\,dl = m\,a\,dl = m\,\frac{du}{d\tau}\,dl = m\,u\,du,$$

whence it follows, by integrating under the assumption that $E_K = 0$ when $u = 0$, that $E_K = \frac{1}{2}\,m\,u^2$. If then the unit of energy is to be defined in terms of kinetic energy, and is to have the same magnitude as when defined in terms of force in the manner just described, it must, as was done in § 26, be defined as *twice* the energy possessed by a mass of one gram when moving with a velocity of one centimeter per second; for it follows from the last equation that $E_K = \frac{1}{2}$ when $m = 1$ and $u = 1$.

30. **The Factors of Surface, Volume, and Elastic Energies.**— Since changes in cohesion and disgregation energies, the forms of energy which are associated with the particles of bodies, can not as a rule be separately measured, attention will be here confined to the relation between the external changes in bodies, that is, between the changes in their surface, volume, and form, and the energy-changes that may be thereby produced in the surroundings. In accordance herewith, it is convenient, as stated in § 25, to employ the terms *surface*, *volume*, and *elastic energies*, to designate the powers of doing external work which bodies possess in virtue of their tendency to undergo changes in surface, volume, and form, respectively. These energies are therefore measured by placing the changes in them accompanying a definite change of surface, volume, or form, equal to the maximum quantity of external work which the change can produce. This quantity of work is, moreover, usually determined by first measuring the force that must be externally applied to the body, in order to compensate the internal force outwardly manifested by it and thus prevent the change from taking place, and then multiplying this external force by the distance through which it is displaced.

It is evident, when a definite change in surface, volume,

or form takes place under this condition of substantially compensated external and internal forces, that the maximum amount of work is obtained from the change : for, if the external force applied were not less in value by at least an infinitesimal amount than the internal force, the change could not take place; if, on the other hand, it were less by a finite amount, the external force displaced, and therefore the work done, would be less than it might be. A similar consideration will show that this maximum quantity of work is substantially identical with the minimum quantity of work by the expenditure of which the reverse change in the surface, volume, or form of the body can be brought about.

It will be clear from these statements that a decrease in the surface, volume, or elastic energy of a system is not necessarily accompanied by the production of an equivalent quantity of work, or indeed of any quantity of work, in the surroundings, since the internal force may be entirely uncompensated, as in the expansion of a gas into a vacuum, or the release of a stretched spring. It is true, moreover, that the decrease in the quantities of these energies, except in the case in which the maximum amount of external work is done, is in general not accompanied by an equivalent increase in the quantity of *any* form of energy, the deficit of work not being compensated by a corresponding production of heat : thus, it will be seen later that in the expansion of a perfect gas into a vacuum, there is not only no production of work, but also none of heat ; yet the volume energy of the gas, or its power of doing external work in virtue of its tendency to undergo volume-changes, has obviously decreased. This apparent contradiction with the First Law of Energetics disappears when it is recognized that quantities of surface, volume, or elastic energies do not have the same significance as do quantities of one of the *forms* of energy, such as kinetic, gravitation, or cohesion energy, whose disappearance is necessarily attended by the appearance of an equivalent

quantity of some other form of energy; for quantities of the first-named energies are defined to be those portions of the total internal energy of bodies which represent the power of producing external work when changes in the surface, volume, or form of the bodies take place; and a decrease in this specific power in the body is not necessarily accompanied by a corresponding decrease in its power of producing those other effects which are a measure of its total internal energy. This distinction will become clearer in connection with the discussion of the Second Law of Energetics.

As has been already stated, the surfaces of liquids tend to diminish in extent and are capable of doing work in virtue of this tendency; they possess, therefore, surface energy. Changes in the quantity of this energy are readily measured in the case where a surface changes in extent in one direction only. Consider, for example, that a surface having the length l_x in one direction, and the length l_y in a direction at right angles to the first, is increased in its extent in the latter direction by an amount dl_y, and that the external force F_l acting in this direction must be applied to the line l_x at right angles to it, in order to compensate the internal surface-force F_s acting upon that line in the opposite direction, and to cause the extension of surface to take place. The surface-force acting upon the unit of length, which force is called the *surface-tension* γ, is then F_s / l_x; and the change of surface ds is $l_x\, dl_y$. The work $(-dW)$ done upon the surface, or the increase in the surface energy dE_s, is then given by the equations:

$$-dW = dE_s = F_l\, dl_y = F_s\, dl_y = \gamma\, l_x\, dl_y = \gamma\, ds;$$

that is, it is equal to the product of the surface-tension into the increase of surface produced.

This resolution of surface energy into factors is an application of the equation $dE = i\, dc$ to a case where i and dc are first determined, the energy-change being defined to be equal to their product.

A concrete illustration involving the principle of one of

the common methods by which surface-tension is experimen-
tally determined will serve to make clearer its nature and the
preceding considerations in regard to it. Consider, as is
represented in Figure 2, a cylindrical tube of small diameter
to be placed in a vertical position with its lower end dipping
into a liquid contained in a larger vessel, the inner walls of
the tube having been previously wet with the same liquid.
As a result of the tendency of the liquid's surface to de-
crease, the liquid rises in the tube ; for thereby the free
surface of the liquid layer adhering to the walls is caused
to disappear up to the height to which the liquid rises. The
liquid column will evidently continue
to rise until the constant surface-force
which is raising it is exactly compen-
sated by the force of gravity acting
downward upon the raised weight of
liquid. Let the radius of the tube be
r and the height to which the column
finally rises be h ; let also, as usual, the
mass, volume, and density of the raised
column of liquid be m, v, and D, and
the acceleration due to gravity be g.
Then the surface-force F_s is expressed
by the equation :

$$F_s = \gamma l = 2 \pi r \gamma,$$

FIG. 2.

since the line l upon which the surface-force is acting is the
inner circumference $(2 \pi r)$ of the tube. Moreover, the force
of gravity F_G acting upon the raised liquid has the value :

$$F_G = m g = v D g = \pi r^2 h D g,$$

since $\pi r^2 h$ is the volume of a cylinder of radius r and height
h. Therefore, when $F_s = F_G$,

$$\gamma = \tfrac{1}{2} g r h D.$$

Hence, by measuring the density of a liquid and the height
to which it rises in a tube of known radius, its surface-tension
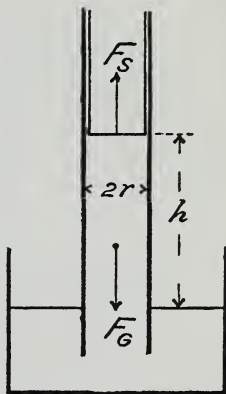
can be determined. This height is evidently directly proportional to the surface-tension of the liquid, and inversely proportional to its density and to the radius of the tube. By reason of this last fact, it is only in capillary tubes that considerable rises are observed.

In the general case, in which a surface increases in extent in any number of directions, it is still true that $dE_s = \gamma\, ds$. For then the surface-change ds, represented in Figure 3 by the area between the outer and inner curves, can be considered equal to the sum of a very large number of infinitesimal surface-changes of the next higher order, each of which is the product of a line of infinitesimal length dl_x by the distance dl_y through which it is displaced; that is, $ds = \Sigma\, (\,dl_x\; dl_y\,)$. If now the force acting on the line dl_x is dF_s, the energy-change when the line is displaced through the distance dl_y is evidently $(\,dF_s\; dl_y\,)$, and the total energy-change dE_s corresponding to the total surface-change ds is the sum of these elementary energy-changes; that is, $dE_s = \Sigma\, (\,dF_s\; dl_y\,)$. Since the surface-tension, the force acting on a line of unit-length, is known to have the same value in all directions within the surface, it is evidently true for each force-element that $dF_s = \gamma\, dl_x$, where γ is constant. It follows, therefore, that :
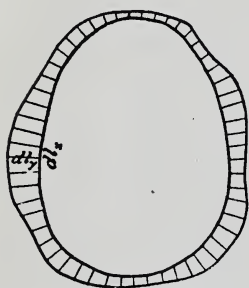
$$dE_s = \Sigma\, (\gamma\, dl_x\; dl_y) = \gamma\, \Sigma\, (dl_x\; dl_y) = \gamma\, ds.$$

It is found, experimentally, that the surface-tension varies greatly with the chemical nature of the liquid, and that it decreases rapidly with rise of temperature, but that it is not affected by variations in the extent of the surface. In view of this last fact, when the temperature is constant, the equation $dE_s = \gamma\, ds$ can be integrated, regarding γ as constant, with the result :

FIG. 3.

$$E_{s_2} - E_{s_1} = \gamma \, (s_2 - s_1),$$

where s_2 and s_1 represent two different extents of surface, and E_{s_2} and E_{s_1}, the corresponding values of the surface energy.

Since surface-tension is defined to be the surface-force exerted upon a line of unit-length, it is measured in the centimeter-gram-second system in dynes per centimeter.

Volume energy is possessed by bodies in all three states of aggregation, but the term is applied to the energy of solid bodies only when it is manifested equally in all directions; in other cases the term elastic energy is used. Volume energy is exhibited in a variety of phenomena, and many of these are of great physical and chemical impor-tance. As examples of changes by which external work is done as a result of a change of volume may be mentioned the expansion of a gas when the external pres-sure upon it is sufficiently reduced, the pro-duction of a volume of gas by a chemical reaction against the atmospheric pressure, and the vaporization of a liquid under its constant vapor-pressure. In all such cases the decrease of the volume energy of the body is by definition equivalent to the maximum amount of work that can be obtained when the change in volume takes place.
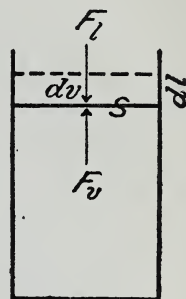
FIG. 4.

Changes in the quantity of volume energy are most readily calculated in the case where the volume undergoes a change in dimensions in one direction only. Suppose, as is represented in Figure 4, that a liquid or gaseous substance contained in a cylinder is enclosed by a movable piston of cross-section s, and that a force F_l is exerted upon this piston, for example, by a weight placed upon it, just sufficient to com-pensate the expansive force F_v of the body and prevent its expansion. Suppose now that the external force be reduced by an infinitesimal amount and that the piston rises through a distance dl. The increase of volume dv is then $s \, dl$, and

the expansive force acting upon the unit of surface, which force is called *pressure p*, is F_v / s. The work dW done by the body, or the decrease in its volume energy $(-dE_v)$, is therefore given by the equations :

$$dW = -dE_v = F_l \, dl = F_v \, dl = p \, s \, dl = p \, dv \, ;$$

that is, it is equal to the product of the pressure into the infinitesimal increase of volume that takes place.

In the general case in which the volume increases in dimensions in any number of directions, it is still true that $-dE_v = p \, dv$. This may be demonstrated by a proof analogous in every respect to that by which the equation $dE_s = \gamma \, ds$ was shown to be an entirely general one : for in this case the volume-change dv can be considered equal to the sum of a large number of infinitesimal volume-changes of the next higher order, each of which is the product of a surface of infinitesimal area ds into the distance dl through which it is displaced; and, in the analogous calculation of the accompanying energy-change, the pressure, like the surface-tension, may be considered to have the same value in all directions.

The general expression for the decrease in volume energy E_v of a body that undergoes a change of volume from v_1 to v_2, or the maximum amount of work W that can be done by it, is therefore :

$$W = E_{v_1} - E_{v_2} = \int_{v_1}^{v_2} p \, dv.$$

If the pressure is constant during the change of volume, this equation becomes :

$$W = E_{v_1} - E_{v_2} = p \, (v_2 - v_1).$$

If, however, the pressure varies, as is frequently the case, it is evidently necessary to know the functional relation between pressure and volume before the integration can be carried out. This will be illustrated in the later paragraphs of this section, in which some applications of the general equation are presented.

In the centimeter-gram-second system pressure is expressed in dynes per square centimeter. Other units that may be employed for its measurement, the gram per square centimeter, the height in centimeters of a compensating mercury column at 0°, and the atmosphere, have been referred to above. Since the density of mercury at 0° is 13.596 (almost exactly **13.6**), a column of it one centimeter in height exerts a pressure of 13.596 grams per square centimeter; and at the sea-level in latitude 45°, where the value of g is 980.7, this is equal to a pressure of 980.7 × 13.596 or 13333 dynes per square centimeter. One atmosphere, which is by definition equal to a pressure of 76 cm. of mercury, is therefore equal to 76 × 13333 or 1 013 300 dynes.

The most important cases in which a change of volume takes place under a constant external pressure are those in which a pure liquid or solid substance vaporizes at a constant temperature against an external pressure made substantially equal to its vapor pressure, and those in which a system expands against the prevailing atmospheric pressure, owing either to a rise in its temperature or to the occurrence of some chemical reaction within it; or those in which a reversal of these changes takes place. In such cases the work done or the decrease of volume energy is found by substituting in the expression $p\,(v_2 - v_1)$ the values of the constant pressure and of the final and initial volumes of the system. The case where the change consists in the production of a gas from liquid or solid substances deserves, however, special consideration. If the volume of the gas produced be v and the final and initial volumes of the non-gaseous part of the system be V_2 and V_1, the work done,

$$W = p\,(v + V_2 - V_1).$$

If the pressure is small, the change in volume of the non-gaseous part of the system can be neglected without giving rise to any considerable error in the calculated amount of work; for this volume-change is then very small in comparison with the volume of the gas produced. In this case,

$$W = pv = NRT,$$

where N is the number of mols of gas produced. It is thus seen that the work done is the same for one mol of any gas, is independent of its pressure or volume, and is proportional to the absolute temperature.

In order to calculate by this equation the numerical value of the work done, it is necessary to know that of the gas-constant R expressed in ergs, joules, or calories. Its value was shown in § 24 to be 0.0820 when the pressure is expressed in atmospheres and the volume in liters : since one atmosphere is equal to 1 013 300 dynes and one liter to 1000 ccm., it follows that :

$$R = 0.0820 \times 1\,013\,300 \times 1000 = 8.31 \times 10^7 \text{ ergs} =$$
$$8.31 \text{ joules} = (8.31 \,/\, 4.184) \text{ cal.} = 1.986 \text{ cal.}$$

Therefore, the numerical value of the work done is in general :

$$W = 8.31 \times 10^7 NT \text{ ergs} = 8.31 NT \text{ joules} = 1.986 NT \text{ cal.}$$

It is convenient to remember that the value of the work done is very nearly **2** T calories for each mol of gas produced. If a gas condenses to a liquid, or is absorbed by a reacting mixture, the work done has, of course, the same numerical value, but a negative sign. — The magnitude of the error caused by neglecting the change in volume of the liquid may be illustrated. One gram of water at 100° has in the liquid state a volume of 1.043 ccm., and in the form of saturated vapor (at one atmosphere's pressure) a volume of 1661 ccm. The former volume is thus only 0.06 per cent. of the latter. Since the volume of liquids is but slightly affected by pressure, while that of gases is nearly inversely proportional to it, the error in neglecting the former volume increases or decreases nearly proportionally with the increase or decrease of pressure.

A very important case of expansion in which the pressure is variable is that in which the temperature of a quantity of a gas remains constant, and its volume is varied (from v_1 to v_2). The pressure of the gas, assuming that its value is not

too great, then varies continuously (from p_1 to p_2) in accordance with Boyle's Law, and has for any volume v the value $p = NRT/v$. If now the pressure of the gas is compensated by an externally applied pressure kept always substantially equal to its own, the work done,

$$W = \int_{v_1}^{v_2} p \, dv = NRT \int_{v_1}^{v_2} \frac{dv}{v} = NRT \log \frac{v_2}{v_1};$$

or, since by Boyle's Law, $v_2 / v_1 = p_1 / p_2$,

$$W = NRT \log \frac{p_1}{p_2}.$$

Substituting as before the appropriate numerical value of R, an expression for the work done in ergs, joules, or calories is obtained. For use in numerical computations the expression may be further simplified by multiplying the value of R by 2.303 and substituting ordinary for natural logarithms, since in general, $\log_{10}[\ ] = 2.303 \log[\ ]$. For example, in order to calculate the work done in joules when one gram of oxygen at 20° and a pressure of three atmospheres expands against an external pressure constantly kept substantially equal to its own until its pressure becomes one atmosphere, we place in the last equation, $N = m / M = 1 / 32$; $R = 8.31$; $T = 273 + 20$; and log $(p_1 / p_2) = \log 3 = 2.303 \log_{10} 3 = 2.303 \times 0.4771$; whereby we obtain $W = 83.6$ joules. If in this example the words "one liter of any gas" were substituted for "one gram of oxygen," the problem would be most readily solved by putting $NRT = pv$, substituting for p its value in dynes ($3 \times 1 013 300$) and for v its value in cubic centimeters (1000), multiplying the result by log 3 as before, and reducing to joules by dividing by 10^7.

One other case of expansion at constant temperature under a variable pressure, that of a liquid which has been compressed by the application of external force, will be briefly considered. Such a liquid is found to exert a pressure which is approximately proportional to the fractional decrease in

its volume already produced; that is, $p = \dfrac{1}{\kappa} \dfrac{V_0 - V}{V_0}$, where V_0 is the volume of the liquid when under no pressure, V its volume when under the pressure p, and κ is a quantity, defined by this equation and known as the *compression-coefficient*, which is nearly constant for moderate changes of pressure, but variable with the chemical nature of the substance and the temperature. By substituting this value of p in the general equation, $dW = p\,dv$, and integrating, the work corresponding to any definite volume-change is determined. It is customary, it may be added, to use the atmosphere as the unit of pressure in stating the numerical value of the compression-coefficient.

The simplest case of elastic energy, and the only one that will be here referred to, is that shown by a bar of uniform cross-section which is stretched or compressed by the application of forces at its ends ; for example, that shown by a metal wire fastened at its upper end and supporting at its lower end a heavy weight. In such a case, which is analogous to that in which surface energy causes a decrease of surface in only one direction, the increase in elastic energy dE_ε is to be regarded as the product of a force, called the *elastic force* F_ε, into the increase in length dl. That is, $dE_\varepsilon = F_\varepsilon\,dl$. The elastic force tending to cause the bar or wire to become shorter is measured by the external force that must be applied in order to compensate this tendency. Its value is found to be proportional to the ratio of the increase in length $l - l_0$ that the external force has already produced in the bar to its original length l_0, inversely proportional to the cross-section s of the bar, and variable with the chemical nature and physical condition of the substance composing it. The stated proportionality holds true, however, only when the fractional increase in length has not exceeded a certain value known as the *elastic limit*. These laws of the elastic force developed under the conditions stated are expressed by the equation, $F_\varepsilon = \epsilon\, s\, \dfrac{l - l_0}{l_0}$, where ϵ

is a quantity, known as the *modulus of elasticity*, constant
with reference to variations in the length and cross-section of
the bar, but varying with its chemical composition and physical
condition, and fully defined by the equation itself.   By substi-
tuting this value of F_ε in the preceding differential equation,
and integrating, the decrease in elastic energy, or the maxi-
mum work that can be obtained, when a definite change in
the length of the bar takes place, is determined.

**31. Electricity and Magnetism. Coulomb's Law.
Electric Currents.** — Just as the manifestations of gravita-
tion and kinetic energies lead us to assign to bodies con-
stant inherent properties which express their capacity for
those energies, and to conceive an entity, matter, which gives
rise to those properties (§ 7), so the phenomena connected
with electrical and magnetic energies lead to the conclusion
that the bodies manifesting them have temporarily acquired
a definite property upon which in part depends the quantities
of these energies which the bodies possess, and lead further to
the conception of quantities, called electricity and magnetism,
which by their temporary association with matter give rise
to this property in bodies.   Hence, these concepts have a
fundamental relation to electrical and magnetic energies
similar to that which matter has to gravitation and kinetic
energies.   Therefore, the important principles relating to
them will be first considered.

When a piece of glass and a piece of resin are rubbed
or pressed together and are then separated, they are found
to have acquired the property of attracting each other.
When another piece of glass and another piece of resin
are rubbed and separated, it is found that the two pieces of
glass or the two pieces of resin repel each other, and that
either piece of glass attracts either piece of resin.   When,
moreover, two other bodies of different natures are rubbed
and separated, it is often found that they attract each
other, and that then one of them always possesses the prop-
erty of attracting a piece of glass and repelling one of resin

which have been previously rubbed together, and that the other body possesses the opposite property. The degree of the attraction or repulsion is also found, in general, to be different in the case of the different bodies. It is evident, then, that they have acquired distance energy with respect to one another, and that each of them separately has acquired a property which in part determines what energy it possesses with reference to any one of the other bodies, and, further, that this property not only varies in magnitude, but is, in the different cases, of two opposite kinds with respect to the direction of the effects corresponding to it. Hence, in order to express the existence and directional character of this property in bodies, it is assumed that there are *two kinds of electricity*, called positive and negative electricities ; and those bodies which have acquired the property of attracting each other are said to be *electrified* or *charged* with the opposite kinds of electricity, and those which repel each other, with the same kind of electricity. It is further agreed, entirely arbitrarily, to designate the electricity upon glass which has been rubbed with resin as *positive electricity*, and that upon the resin as *negative electricity*, and to designate all other charges of electricity, in whatever manner produced, as positive or negative, according as they repel or attract the charge upon the glass, or attract or repel the charge upon the resin.

It is agreed, moreover, to measure *quantities of electricity* by placing them proportional to the forces of attraction or repulsion which indefinitely small bodies charged with them exert upon one another when the bodies are at a definite distance and are separated by a definite medium. And correspondingly, the *C. G. S. electrostatic unit of electricity* is defined to be that quantity of electricity which, when placed in air under the normal conditions at a distance of one centimeter from an equal quantity of the same kind of electricity, repels it with a force of one dyne.

Of the important principles in regard to quantities of

electricity the following one may be first stated : *The appear-
ance of a quantity of one kind of electricity at any place is
always accompanied by the appearance of an equal quantity
of the other kind of electricity at some other place.* If, as is
customary, quantities of positive and negative electricities are
considered to be positive and negative numerical quantities,
respectively, this principle can also be stated as follows :
*The algebraic sum of all quantities of electricity developed
by any process whatever is equal to zero.* This law may
be demonstrated by experiments like the following : if two
disks, one of sealing-wax and one covered with flannel, be
rubbed together, and either of them be then separately in-
serted within a hollow metal vessel connected with a gold-
leaf electroscope, it is found that the gold leaves diverge,
owing to their electrification by the effect known as induc-
tion ; if, however, both of the disks be simultaneously inserted
within the vessel, it is found that no divergence takes place,
showing that the effects of the opposite electricities on the
two disks just neutralize each other, and therefore that
the quantities of them are equal.

Another fundamental principle in regard to quantities
of electricity is that relating to their attraction and repulsion.
This may be stated as follows : *Every elementary quantity
of electricity repels every other such quantity of the same
kind, and attracts every other such quantity of the opposite
kind, with a force varying directly as the product of those
quantities, inversely as the square of the distance between
them, and specifically with the nature of the dielectric.*
The term *elementary quantity of electricity* is here used to
express an infinitesimal quantity of electricity, or any quan-
tity of it that can be regarded as located at a point. The
term *dielectric* is the one commonly employed to designate
the non-conducting medium separating the two quantities of
electricity. The first portion of this statement, which asserts
proportionality between the force of attraction or repulsion
and the quantities of electricity, is obviously only a converse

expression of the above-given definition of these quantities. That portion of it which has reference to the influence of distance has been established by experimental investigations, and is known from its discoverer as *Coulomb's Law.*

These principles are expressed by the equation:

$$F_E = - \frac{1}{K} \frac{Q_1 Q_2}{l^2},$$

where F_E is the force of attraction between two quantities of electricity, Q_1 and Q_2, located at points at a distance l from each other, and K is a positive quantity, known as the *dielectric constant,* which is constant with reference to variations of Q_1, Q_2, and l, but variable in a high degree with the nature of the dielectric. (Thus, its value is 80 times as great for water at 18° as it is for air.) In this expression the numerical values of Q_1 and Q_2 are to be taken positive or negative according as they represent quantities of positive or negative electricity : that of F_E then becomes positive or negative according as those of Q_1 and Q_2 have unlike or like signs, a negative value of F_E evidently signifying a repulsion.

The increase in distance energy dE_l accompanying an increase in distance dl between two elementary quantities of electricity is therefore expressed by the equations:

$$dE_l = F_E \, dl = - \frac{Q_1 Q_2}{K} \frac{dl}{l^2} = - \frac{Q_1 Q_2}{K} d \left(- \frac{1}{l} \right)$$

The close analogy between these expressions and those for gravitational force and energy (§ 29) is apparent. The quantities Q_1, Q_2, evidently have ·to electrical distance energy on the one hand, and to the concept of electricity on the other, a relation entirely similar to that which the quantities m'_1, m'_2, have to gravitation energy and to the concept of matter.

Coulomb's Law was originally derived and verified by measuring the forces of attraction and repulsion between two small electrified bodies by means of the so-called torsion-balance, in which a gilded pith-ball, attached at the end

of a light horizontal arm that is suspended at its center by a vertical wire, is electrified and placed at varying distances from a small electrified metal sphere fixed in position ; the relative values of the electrical force being measured by noting the angle through which the top of the wire must be turned, in order that its torsion may just compensate the tendency of the two bodies to approach or recede from each other. The attraction or repulsion of electrified bodies whose dimensions are considerable in comparison with the distance between them cannot, however, be so simply expressed, not only because the charges, not being located at definite points, are not at any one definite distance from each other, but also because, by reason of the phenomenon of electrical induction, the charges mutually influence the distribution of each other upon the surfaces of the bodies, so that the elementary quantities of electricity located at definite points are not the same when the bodies are near each other as they are when the bodies are so distant that no appreciable inductive effect is exerted.

The above-stated law relating to the attraction and repulsion of elementary quantities of electricity also determines the distribution of electricity upon bodies ; thus, the principles that it resides entirely upon their surfaces and in greatest quantity upon those parts where the curvature of the surface is greatest, are consequences of it. Conversely, from the distribution as experimentally determined the law itself has been mathematically derived ; and it is in this way that its exactness has been most rigidly demonstrated.

In closing the consideration of statical charges of electricity, a few terms in common use may be defined. The quantity of electricity on the unit of surface is called the *surface-density* of the charge. The space surrounding an electric charge and in such proximity to it that an appreciable effect would be exerted upon an electrified body that might be placed there, is called an *electric field*. The force that would be exerted at any point of an electric field upon a unit-

charge of positive electricity considered to be placed there without itself influencing the field, is called the *intensity* or *strength of field* at that point. The lines in an electric field which represent the direction in which such a charge would tend to move are called *lines of force.* By a pure convention it is agreed to consider to be drawn through any section of the field of unit-area that is at right angles to the lines of force a number of lines equal to the intensity of field in that section ; and intensity of field is often numerically expressed by stating the *number of lines of force per square centimeter,* in correspondence with this convention.

Some important principles relating to magnetism will be next presented. When two bars of steel are separately subjected to certain influences — for example, when they are systematically rubbed with a lode-stone or placed within a helical coil of wire through which an electric current is passing — the corresponding ends of the two bars are found to repel each other and the opposite ends to attract each other with forces varying within certain limits with the influence to which they have been subjected. Such steel bars, and other bodies whose opposite parts possess the property of attracting and repelling the ends of such bars, are said to be *magnetized;* and it is conceived that upon the ends are present quantities of two opposite *kinds of magnetism.* The points at which the resultants of the attracting and repelling forces act, and at which the magnetism may be assumed to be located, are called the *magnetic poles.* When a magnetized bar or needle is suspended at its middle point so as to swing freely in a horizontal plane, it is found that it sets so as to point nearly north and south. That pole that turns towards the north is called the *north pole* of the magnet ; that towards the south, the *south pole :* and the magnetism in a north pole is called *north* or *positive magnetism ;* that in a south pole, *south* or *negative magnetism.*

The principles stated above in regard to the measurement and the attraction and repulsion of quantities of elec-

tricity, and in regard to the simultaneous development of opposite kinds of it, all apply to quantities of magnetism; it being only necessary in the statements of them to substitute the word magnetism for the word electricity. To the statement of the last-mentioned principle may be added the limitation that the equal quantities of the two kinds of magnetism are always developed in different parts of the same continuous body; that is, no body ever contains an excess of either kind of magnetism: thus, in this respect, magnetism differs from electricity. The absolute unit of magnetism, defined in complete analogy with the unit of electricity, has no specific name, but is known as the *C. G. S. unit of magnetism.* The constant determined by the nature of the intervening medium, occurring in the expression of Coulomb's Law, is, in the case of magnetism, known as the *magnetic permeability;* its value for air under the normal conditions, like that of the dielectric constant, is by definition unity. The terms *field, intensity* or *strength of field,* and *lines of force* are used in the same sense in connection with magnetism as in connection with electricity; the word magnetic or electric being added when it is necessary to discriminate. One other term in very common use may also be here defined; this is the term *strength of pole,* which is used as the equivalent of the expression quantity of magnetism in the pole.

Although electricity and magnetism have many characteristics in common, it is to be noted that stationary charges of electricity exert no attraction or repulsion on magnetic poles. They differ from one another also in that electricity is capable of flowing under suitable conditions from one body to another, while magnetism is not. This flow of electricity will be next considered.

If two electrified bodies are connected by a wire, in general a momentary flow of electricity takes place from one body to the other, as is shown by the redistribution of the electricity upon the two bodies. If new quantities of electricity are continuously imparted to the one body and removed

from the other body, for example, by connecting them with the terminals of an electrical machine, or, better, with those of a voltaic cell, the connecting wire acquires certain new properties, and is said to be traversed by a *current of electricity* or an *electric current*. One of these properties of the wire is that of exerting upon a magnetic pole a force tending to move it in a direction at right angles to the plane embracing the wire and the pole ; and it is agreed to measure electric currents by placing them proportional to this force under specified conditions. Namely, the *C. G. S. electro-magnetic unit of current* is the current which, flowing in a conductor of the form of a circular arc one centimeter long, with a radius of one centimeter, acts with a force of one dyne on a magnetic pole of unit-strength placed at the center of the circle. The *C. G. S. electro-magnetic unit of electricity* is then defined to be the quantity of it which passes between two points in one second when the C. G. S. electro-magnetic unit of current is flowing between them. Therefore, in general, designating the current by i, and the time during which it flows by τ, the total quantity of electricity ϱ which passes in that time is given by the equation, $\varrho = i\tau$. It should be added that it is agreed to understand by the *direction of the current* the direction in which positive electricity, as electrostatically defined, is flowing.

The general law governing the force F exerted by a length l of a circular arc, of radius r, through which a current of strength i is flowing, upon a magnetic pole of strength m placed in air at the center of the circle, is expressed by the equation : $F = m\,i\,l\,/\,r^2$. The direction in the line perpendicular to the plane of the circuit and magnetic pole in which the force acts, is determined both by the direction of the current and the sign of the magnetism in the pole, in a manner that need not be here specified. This action exerted on quantities of magnetism by electric currents shows that a magnetic field is produced in the neighborhood of the current. Thus, it is seen that, though, as stated above, there are no effects exerted

between magnetic poles and stationary electric *charges*, yet there are important relations between the former and electric *currents*.

The ratio of the electromagnetic to the electrostatic unit of electricity is evidently one of the most fundamental constants connected with electrical phenomena, since it makes it possible to bring the effects of statical charges into quantitative relations with those of electric currents. Its numerical value has been found to be 3.00×10^{10} by means of direct experimental comparisons of these two kinds of effects. The very high value of this constant shows that quantities of electricity which in the form of statical charges exert a considerable force upon one another give rise to only an extremely slight electromagnetic force when in the form of a current; moreover, it is true in general that the quantities of electricity concerned in most electrostatic phenomena are almost inappreciable in comparison with those ordinarily involved in the case of electric currents. Incidentally, it may be mentioned that the value of the ratio of the two units has been found to be identical, within the experimental error, with the velocity of light — a remarkable relation of great theoretical significance.

32. **The Factors of Electrical Energy. Ohm's Law and Joule's Law.** — In the preceding section an expression was given for the change in the electrical energy of two quantities of electricity corresponding to a displacement of one of them in the direction in which the electric force is acting. This is obviously only a special case. In order to express in a general manner the change in electrical energy, — that produced by the displacement of a quantity of electricity in any direction whatever in any electric field whatever, — the change in energy is considered to be the product of two factors: one of these is quantity of electricity, to which under otherwise constant conditions electric force and energy have already been seen to be proportional; and the other is *difference of potential*, which is defined to be that factor with

which the quantity of electricity must be multiplied in order to produce the energy. That is, if a quantity of electricity ϱ when transferred from one point to another in an electric field suffers a change dE in its electrical energy, the difference of potential dv between the two points is defined by the equation, $dv = dE / \varrho$. This method of defining the factors of electrical energy is evidently an application of the general equation, $c = dE / di$, to a case in which c and dE are first independently determined.

In accordance with this equation, the *C. G. S. unit of potential-difference* is the potential-difference that exists between two points when, upon transferring from one of them to the other a unit of electricity, its energy changes by one erg. Corresponding to the electrostatic and electromagnetic units of electricity, there are, of course, two units of potential-difference. It is also agreed to adopt as the *zero of potential* the value of it at a point infinitely distant from the charges producing the electric field, which is practically identical with the value at any point in electrical connection with the body of the earth. By integrating the equation, $dv = dE / \varrho$, under this assumption that the potential is zero when the distance is infinity, we get for the absolute value of the potential v at any point, $v = (E - E_\infty) / \varrho$, where E and E_∞ are the electrical energies at that point and at an infinite distance, respectively. By putting $\varrho = +1$ in this equation, we find that the *potential* at any point of an electric field is mathematically equivalent to the increase in the electrical energy of a unit-quantity of positive electricity when this is transferred from an infinite distance to the point in question. Its numerical value is evidently positive when the energy-increase is positive, and negative when it is negative. This energy-increase, and therefore also the potential, is obviously equal to the external work that must be expended in transferring the unit-quantity of positive electricity from an infinite distance to the point in question.

Since an energy-increase accompanying a decrease of

distance corresponds to a force of repulsion, it is clear that, by reason of the definitions adopted, positive electricity tends to flow from a place at higher to one at lower potential. Negative electricity, on the other hand, evidently will tend to flow from a place at lower to one at higher potential. Potential is therefore the intensity-factor of electrical energy, and it has the peculiarity that a definite difference in its value causes the energy to transfer itself in one direction or the opposite one, according as the electricity involved is positive or negative. Since, however, almost all of the effects produced by the flow of positive electricity in the one direction are identical with those produced by the flow of negative electricity in the other, it is in most cases impossible to determine to what extent the two separate flows are taking place, and it is customary, for convenience sake, to consider that an electric current is wholly one of positive electricity, its magnitude as well as its direction being determined from its effects by attributing these entirely to this kind of electricity.

The relation of quantity of electricity and difference of potential to electrical energy is made clearer by considering the analogy between it and the relation of quantity of water and difference of level to gravitation energy. Water situated at any level above that of the sea possesses a quantity of gravitation energy which is greater, the greater the quantity of water and the greater the difference between the two levels, just as the quantity of electrical energy is greater, the greater the quantity of electricity and the greater the difference of potential. Moreover, in order that there may be a tendency for water to flow from one place to another, there must be a difference of level between the two places, just as there must be a difference of potential at two places in order that there may be a tendency for electricity to flow between them.

In place of the expression difference of potential, it is very common, when electric currents are under consideration,

to use the more general term *electromotive force* (E), which signifies any cause whatever that tends to produce a flow of electricity.

Magnetic energy is resolved into the factors *quantity of magnetism* and *magnetic potential*, which have a significance entirely similar to that of the factors of electrical energy. Quantity of magnetism was considered in the preceding section. Magnetic potential is defined with reference to the transfer of a quantity of magnetism in exactly the same manner as electric potential has been defined with reference to that of a quantity of electricity.

Certain important principles relating to electric currents will be next considered. In order that a current may flow between two points, it is necessary, not only that they be at different potentials, but also that they be connected with each other by a suitable medium. A medium which allows an appreciable current of electricity to flow through it is called an electrical *conductor;* one which does not, a *non-conductor* or *insulator.* In regard to the strength of the current the following general principle, known as *Ohm's Law*, has been derived and thoroughly confirmed by experiment: *When a steady current flows between two points without producing any form of work, its strength (I) varies directly as the difference (E) of the potentials of the points, and specifically with the character of the conductor connecting them.* That is, $I = E/R$, where R is a quantity, called the *resistance* of the conductor, constant with reference to variations of I and E, but varying with the form, chemical nature, and physical condition of the conductor. Since by this equation resistance is defined to be equal to the ratio (E/I) of potential-difference to current when no work is produced by it, the *C. G. S. unit of resistance* is also determined: it is equal to the resistance of a conductor through which a C. G. S. unit of current flows when there is a difference of a C. G. S. unit of potential at its ends. The resistance of a homogeneous conductor of uniform dimensions is found to be proportional to its length (l) and

inversely proportional to its cross-section (s) ; that is, $r = \underline{r}\, l\, /\, s$, where $\underline{r}$ is a quantity, designated the *specific resistance* or the *resistivity* of the substance, which is defined by this equation, and which is, therefore, in terms of the units commonly employed, the resistance of a prism of it one centimeter in length and one square centimeter in cross-section. Its value varies not only with the chemical nature of the substance, but also with physical conditions, especially with the temperature. It is often more convenient to employ in place of the resistance of a conductor the reciprocal of its value, which is called the *conductance* (L) ; this is evidently equal to the ratio of the current to the potential-difference ; that is, $L = 1\, /\, r = I\, /\, e$. The conductance of a homogeneous conductor of uniform dimensions is directly proportional to its cross-section and inversely proportional to its length ; that is, $L = \underline{L}\, s\, /\, l$, where $\underline{L}$ is the *specific conductance* or the *conductivity* of the substance, or the conductance of a prism of it one centimeter in length and one square centimeter in cross-section.

When work of any kind is produced by the passage of a current (for example, when mechanical energy is produced by a motor, when electrical energy is produced in another conductor by a transformer, or when chemical energy is produced by a chemical decomposition), a *counter* or *back electromotive force* is developed in the circuit, and the current-strength is correspondingly reduced. The statement of Ohm's Law applicable to this general case is that *the current-strength is equal to the ratio of the algebraic sum of all the electromotive forces to the sum of all the resistances in the circuit.* That is, $I = \Sigma e\, /\, \Sigma r$. For example, suppose that a storage battery, whose internal resistance is r_1, and which produces an electromotive force e_1, is placed in a circuit with a motor of resistance r_2 and an electrolytic cell of resistance r_3, the whole being connected by metallic conductors of resistance r_4 ; suppose further that the activity of the motor gives rise to a back electromotive force e_2, and that the chemical decomposition in the cell produces a back electromotive force e_3 :

the strength $\imath$ of the current flowing through the circuit is then given by the equation, $\imath = \dfrac{E_1 - E_2 - E_3}{R_1 + R_2 + R_3 + R_4}$.

When a quantity of electricity ϱ flows between two points and thereby undergoes a fall of potential E, its electrical energy decreases by an amount equal to the product $E\varrho$, and must appear as some other form of energy, commonly as heat, chemical energy, or mechanical energy, or else as electrical energy in another conductor. If a quantity of heat Q is alone produced, as is the case when the two points are connected by an ordinary metallic conductor, we get by the substitution of the value of E from the equation expressing Ohm's Law:

$$Q = E\varrho = E\imath T = \imath^2 R T.$$

This equation states that *the heat developed in a conductor by the passage of a current which produces no work is equal to the square of the current-strength multiplied by the time during which the current passes and by the resistance of the conductor.* This principle is known as *Joule's Law.* It has received independent confirmation by direct experiments. When the current, resistance, and time are expressed in C. G. S. units, the heat-effect is, of course, expressed in ergs.

When mechanical or electrical work is produced by a current (as in an electric motor or in a transformer), it is found experimentally to be still true that a heat-effect equal to $\imath^2 R T$ is also produced, so that Joule's Law is applicable to this case also. When chemical energy, however, is produced by an electric current (as by the decomposition of a chemical substance), the total heat-effect is not in general equal to $\imath^2 R T$; there are, nevertheless, good reasons for regarding it as the algebraic sum of two separate heat-effects, one of which is equal to $\imath^2 R T$; this is called the *Joule Heat-Effect*, to distinguish it from the total heat-effect. — Consider, for example, the application of these principles to the circuit described above, containing a storage battery, a motor, and an electrolytic cell. If the current $\imath$ flows for a time T, the storage

cell yields a quantity of electrical energy $E_1 I T$. Of this energy, by reason of the resistances, the quantities $I^2 R_1 T$, $I^2 R_2 T$, $I^2 R_3 T$ and $I^2 R_4 T$ are converted into heat in the storage cell itself, the coils of the motor, the electrolytic cell, and the metallic conductors, respectively. The motor takes, in addition, a quantity of energy $E_2 I T$ which is convertible into work. The remainder of the energy $E_3 I T$ is consumed in the electrolytic cell, appearing there in the form of chemical energy (that possessed by the products of the decomposition) and sometimes partly in the form of heat.

In closing the consideration of electrical energy and the relations of its factors, a few words must be added in regard to electrical units. Since many of the C. G. S. units, both in the electrostatic and electromagnetic systems, are of an extremely inconvenient magnitude for the expression of the electrical quantities involved in ordinary work with electric currents, a so-called *practical system* of electrical units has been devised, and this system, or one substantially identical with it, is used almost exclusively both in electrical science and electrical engineering. All the units in this system are exact decimal multiples or submultiples of the corresponding C. G. S. electromagnetic units. They are designated and defined as follows : The unit of current is called the *ampere* and is defined to be one-tenth of the C. G. S. electromagnetic unit of current, which was defined in the preceding section. The unit-quantity of electricity is the *coulomb*, which is the quantity flowing per second when the current is one ampere. The unit of potential is the *volt*, which is equal to the potential-difference between two points when a change of one joule (equal to 10^7 ergs) in the electrical energy attends the passage of one coulomb of electricity between them : it is evidently equal to 10^8 C. G. S. electromagnetic units of potential. The unit of resistance is the *ohm*, which is the resistance of a conductor through which one ampere flows when the potential-difference is one volt : it is equal to 10^9 C. G. S. units of resistance. The unit of conductance is

the *reciprocal ohm,* which is the conductance of a conductor whose resistance is one ohm.   Careful experimental determinations have shown that the ohm is substantially equivalent to the resistance at 0° of a mercury column 106.3 centimeters in length and of a uniform cross-section one square millimeter in area.   It should be added that, in order to facilitate the expression of electrical quantities in terms of these units, certain substantial equivalents of them, more readily realizable experimentally, like the equivalent of the ohm just mentioned, have been recently agreed upon by congresses of electrical engineers and various governments, and have been adopted as new definitions of the electrical units.   These are designated the *international units* (international ohm, international ampere, etc.) in order to distinguish them from the *true units* (true ohm, true ampere, etc.) which were just defined.   It is highly improbable that the values of the international and true units differ in any case by as much as 0.1 per cent.; so that for most purposes they can be regarded as identical.

33. Faraday's Law of Electrolytic Conduction. — Conductors are divided into two classes with reference to the changes that are produced in them by the passage of electric currents.   Those which undergo no changes except such as are produced by a rise in temperature are called *metallic conductors.*   Those in which the passage of a current is attended by a chemical change are called *electrolytes.*   Bodies composed of the various metals and of graphite are examples of good metallic conductors.   Aqueous solutions of salts, bases, and acids, and melted salts at high temperatures, are the most important classes of well-conducting electrolytes.   The most obvious chemical changes attending the passage of a current through an electrolyte are those that take place at the surfaces of the metallic conductors where the current enters and leaves the electrolyte.   The production of such chemical changes by a current from an external source is called *electrolysis.*   The occurrence of such changes, when they

themselves give rise to an electric current, is called *voltaic action*. Those portions of the metallic conductors that are in contact with the electrolyte are called the *electrodes :* the one at which the current leaves the electrolyte, or the one to which the positive electricity flows through the electrolyte, is designated the *cathode* or *negative electrode ;* the other, the *anode* or *positive electrode.*

The chemical changes at the electrodes accompanying the electrolysis of aqueous solutions of salts, bases, and acids consist, in the simplest case, in the precipitation of the metal of the salt or base or of the hydrogen of the acid, or of hydrogen from the water, upon the cathode, and in the precipitation of the halogen or acid radical of the salt or acid or of the oxygen of the base, or oxygen from the water, upon the anode : thus, when a concentrated solution of copper chloride is electrolyzed between carbon electrodes, copper is deposited on the cathode and chlorine is liberated at the anode ; and, when a solution of sodium sulphate, one of sulphuric acid, or one of sodium hydroxide, is electrolyzed between platinum electrodes, hydrogen is liberated at the cathode and oxygen at the anode. In many cases, however, the chemical changes are more complicated, owing to the occurrence of secondary reactions between the primary products of the electrolysis and the substances composing the electrodes or the electrolyte. Thus, when silver nitrate solution is electrolyzed between silver electrodes, the NO_3-radical or oxygen, instead of being precipitated at the anode, attacks the silver of which it is composed and causes an equivalent quantity of it to pass into solution in the form of silver nitrate ; and, when nitric acid is electrolyzed between platinum electrodes, the hydrogen, instead of being set free in the form of gas at the cathode, reduces the nitric acid, and is itself oxidized to water. Furthermore, whenever the electrolysis of a neutral salt (like that of sodium sulphate, for example) is attended by the liberation of hydrogen at the cathode and oxygen at the anode, it is found that a quantity of free base

(sodium hydroxide) equivalent to the hydrogen, and one of free acid (sulphuric acid) equivalent to the oxygen, are present in the portions of the electrolyte surrounding the cathode and anode, respectively, so that, in this case also, the effects observed are those that would result if the metal and acid-radical were the primary products of the electrolysis and these reacted secondarily with the water ; thus, the phenomena observed in the case of the sodium sulphate are those that would arise from the liberation of sodium and the sulphuric-acid radical at the electrodes, and their action upon the water according to the reactions, $2Na + H_2O = 2NaOH + H_2$, and $2SO_4 + 2H_2O = 2H_2SO_4 + O_2$.

In the case of voltaic actions, the chemical changes are of a similar character, most commonly consisting in the solution of the metal composing the anode and in the deposition of another metal or hydrogen on the cathode (the separation of free hydrogen being, however, often prevented by a secondary reaction between it and the electrolyte or the electrode). Thus, in the Daniell Cell, which consists of a copper electrode in a copper sulphate solution and of a zinc electrode in a zinc sulphate solution, the two solutions being in contact and the two electrodes connected by a metallic conductor, the zinc dissolves and the copper precipitates ; and, in the Grove Cell, consisting of a zinc electrode in dilute sulphuric acid and a platinum electrode in strong nitric acid, zinc dissolves at the anode, and the hydrogen primarily produced at the cathode reduces the nitric acid to lower oxides of nitrogen. The chemical changes involved in voltaic actions do not differ, therefore, essentially from those produced by electrolysis, except in the respect that the former tend to take place of themselves, while the latter require the application of electrical energy from an external source.

The amount of chemical change that takes place at the electrodes is determined by the following fundamental principle, which is known from its discoverer as *Faraday's Law : The passage of electricity through an electrolyte is attended*

at each electrode by a chemical change involving a number of chemical equivalents strictly proportional to the quantity of electricity passed through and dependent on that alone.

This law is algebraically expressed by the equation, $q = \underline{q} \nu$, in which q is the quantity of electricity passed through, ν is the number of chemical equivalents involved in the change at each electrode, and $\underline{q}$ is a constant with respect to all variations of the conditions, representing the quantity of electricity producing a chemical change involving *one* equivalent.

The law requires, on account of its generality, illustration by a number of examples. Consider first the electrolysis of a silver nitrate solution between silver electrodes by the passage through it of a definite quantity of electricity, say 1000 coulombs, under variable conditions, assuming, however, that the conditions are always such that the only chemical changes taking place at the electrodes are the deposition of silver upon the cathode and the solution of silver from the anode. Faraday's Law then requires that the quantity of silver deposited on the cathode be the same, and that the quantity dissolved from the anode be the same, whether the silver nitrate solution be concentrated or dilute, whether it be hot or cold, whether the electrodes be so placed in it that its resistance is large or small, and whether the potential-difference at the electrodes, and therefore the current-strength and the electrical energy expended, be greater or less; that is, in spite of all these and other possible variations of conditions, the law requires that whenever 1000 coulombs of electricity have passed through the solution a definite quantity (found to be 1.117 grams) of silver be precipitated at the cathode and dissolved at the anode. Suppose that in a second series of experiments 10 000 coulombs be passed through the solution; then ten times as much silver (11.17 grams) must be deposited and dissolved. Suppose next that, while still passing 10 000 coulombs, the solution be made so dilute or the current-strength so

great in proportion to the electrode-surface that hydrogen is deposited with the silver upon the cathode : the law requires in this case that the sum of the number of equivalents of hydrogen and silver be equal to the number of equivalents of silver deposited in the preceding experiments ; thus, if the amount of silver now deposited be 10.00 grams, that is, 1.17 grams or 1.17 / 107.93 or 0.01084 equivalents less than before, this deficit in silver must be made up by the liberation of an equal number of equivalents of hydrogen gas, that is, since its equivalent weight is 1.008, of 0.01093 grams of it. Consider next that the same current traverses in series the following solutions placed between platinum electrodes : sulphuric acid (H_2SO_4), silver nitrate ($AgNO_3$), mercurous sulphate (Hg_2SO_4), mercuric bromide ($HgBr_2$), gold chloride ($AuCl_3$), and platinic chloride ($PtCl_4$) ; that only a single chemical change takes place at the electrodes in each solution — the precipitation of hydrogen or the corresponding metal at the cathode, and of oxygen or halogen at the anode ; and that the current is continued till 1.008 grams of hydrogen, one equivalent weight, have been liberated from the sulphuric acid solution.   It follows then from Faraday's Law that one equivalent weight of each of the metals and of oxygen or halogen will also be deposited ; namely, since the combining weights (see § 16) corresponding to the above-given formulas are, Ag = 107.93, Hg = 200.0, Au = 197.3, Pt = 195.2, O = 16.00, Br = 79.96, and Cl = 35.45, and since the equivalent weights in the different cases are evidently represented by 1Ag, 1Hg, $\frac{1}{2}$Hg, $\frac{1}{3}$Au, $\frac{1}{4}$Pt, $\frac{1}{2}$O, 1Br, and 1Cl, the result of the electrolysis is the precipitation of 1.008 grams of hydrogen and 8.00 of oxygen from the sulphuric acid, of 107.93 of silver and 8.00 of oxygen from the silver nitrate, of 200.0 of mercury and 8.00 of oxygen from the mercurous sulphate, of 100.0 of mercury and 79.96 of bromine from the mercuric bromide, of 65.77 of gold and 35.45 of chlorine from the gold chloride, and of 48.80 of platinum and 35.45 of chlorine from the platinic chloride.   Consider finally the

application of the law to the voltaic actions taking place in the Daniell Cell when a quantity of electricity is produced by it which deposits 107.93 grams or one equivalent of silver from a silver nitrate solution placed in the circuit in series with the cell. Under these circumstances, according to Faraday's Law, one equivalent of zinc, equal to $\frac{1}{2}$Zn or 32.70 grams, will dissolve from the anode of the cell, and one equivalent of copper, equal to $\frac{1}{2}$Cu or 31.80 grams, will precipitate upon its cathode.

Although numerous determinations have been made which prove the validity of Faraday's Law as an approximation, it has been found very difficult to test experimentally the exactness of it, owing to the impossibility of completely preventing secondary and subordinate reactions at the electrodes, such as the liberation of small amounts of hydrogen at the cathode in the precipitation of metals. A careful study of the best conditions for eliminating such secondary actions has been made in the case of the electrolyses of copper sulphate and silver nitrate solutions, however; and the ratio of the weights of copper and silver precipitated under these conditions by the same current when passed through the two solutions in series has recently been accurately determined, and found to be 1 / 3.3940. The ratio of the chemical equivalents of these two elements, as determined by the most exact chemical analyses of their compounds, is 107.93 / $\frac{1}{2}$ 63.60, or 1 / 3.3940. The two ratios are therefore identical, as Faraday's Law requires.

The quantity of electricity which produces at each electrode a change involving one chemical equivalent, that is, the numerical value of the fundamental constant ϱ in the algebraic expression of Faraday's Law, is called the *electrochemical constant*. It has been determined by combining measurements of the quantity of silver precipitated from a silver nitrate solution with measurements of the time and current-strength (made with a galvanometer or electrodynamometer) employed in the precipitation. Its most probable value is **96 600** coulombs.

With the help of this constant the amount of electro-lytic decomposition produced by the passage of any definite quantity of electricity, and also the quantity of electricity produced by a definite voltaic action, can be calculated. For example, suppose it were desired to determine how much bismuth could be precipitated out of a bismuth chloride ($BiCl_3$) solution by passing a current of 2 amperes through it for one hour. In this case, the quantity of electricity passed ($\varrho = iT$) is 2 × 3600 or 7200 coulombs; therefore, the num-ber of equivalents precipitated ($N = \varrho / \varrho$) is 7200 / 96600 or 0.0745, and the number of grams precipitated ($m = NA$) is 0.0745 × 69.33 or 5.167, since the equivalent weight (A) is one-third of the combining weight 208.0 grams, or 69.33 grams.

34.   **Heat Energy.** — Heat energy has been defined to be the form of energy that is manifested when bodies are placed in communication with surroundings of different temperature. Temperature is therefore its intensity-factor, as has been already stated. Its capacity-factor is called *heat-capacity* (H): it is that which determines the quantity of heat (dQ) which produces a definite increase of temperature (dT) in the body or system under consideration; that is, $H = dQ / dT$. This resolution of heat-energy into factors is an application of the general equation $i = dE / dc$ to a case where i and dE are first independently determined.

The heat-capacity of different homogeneous bodies com-posed of the same chemical substance is directly proportional to their masses or weights; that is, $H = \underline{H}m$, where $\underline{H}$ is the heat-capacity of one gram of the substance, which is commonly called its *specific heat*, but which is more appro-priately designated its *specific heat-capacity*. Its value varies with the temperature, but ordinarily only by a small amount.

Since a body may be heated under various conditions, and since its heat-capacity may vary correspondingly, the conditions of heating must be taken into consideration. The two most important cases are that in which the body expands

under a constant pressure, usually the pressure of the atmos-
phere, and that in which the volume of the body is kept
constant by the application of a suitable external pressure.
The corresponding heat-capacities are called the heat-capacity
at constant pressure (H_p) and that at constant volume (H_v).
In the case of solid or liquid bodies, it is always understood,
when not otherwise specified, that the heating takes place
under the constant pressure of the atmosphere. In the case
of gases, the conditions of heating must always be stated.

It is found, however, in some cases — for example, in
that of a solid substance at the temperature of its melting-
point, or of a liquid at that of its boiling-point — that no
change of temperature takes place when heat is imparted to
the body ; but in such cases a change in the body's state of
aggregation occurs, whereby its internal energy increases ;
and the same amount of heat is evolved when the body
returns to its original condition. The heat absorbed in
such changes of state taking place at constant temperature
is called the *heat-effect of the fusion, vaporization, or subli-
mation* (L). That absorbed by the change in state of one
gram of the substance is commonly called the *latent heat,* or
simply the *heat, of fusion, of vaporization,* or *of sublimation,*
($\underline{L}$), of the substance ; but, in accordance with scientific
usage in the case of other specific properties, it is more
rational to designate it the *specific heat of fusion, vapor-
ization,* or *sublimation.* It is understood, when not specified,
that the change in state takes place under the atmospheric
pressure. An analogous phenomenon is the dissolving of
one substance in another ; and the heat absorbed when one
gram dissolves is called the (*specific*) *heat of solution* of the
substance. When not otherwise specified, it is to be under-
stood that the substance dissolves, under the usual conditions,
in such an amount of solvent that a saturated solution is
formed.

Chemical changes attended by heat-effects, as well as
changes in physical state, may, of course, also take place

within a system.   The heat absorbed by a system as the
result of a chemical change in it is called the *heat-effect of the
reaction.*   In order to express this heat-effect as a specific
property of the reacting substances, it is customary in ener-
getic considerations to regard as the *heat of reaction* (q) that
absorbed when the number of mols undergo change that are
represented by the simplest chemical equation that can be
written, using the molecular formulas of the compounds in-
volved and avoiding fractional coefficients.   Thus, by the heat
of reaction or of combination of hydrogen and oxygen is meant
that corresponding to the equation, $2\,H_2 + O_2 = 2\,H_2O$, that
is, that absorbed by the union of 4.03 grams of hydrogen with
32.00 grams of oxygen.

   In the case where a system undergoes the same change
in state (whether physical or chemical) at two different tem-
peratures, and no external work is done, the First Law of
Energetics gives a simple relation between the quantities of
heat (Q_{T_1} and Q_{T_2}) absorbed by the change at the two tem-
peratures (T_1 and T_2) and the mean values between those
temperatures of the heat-capacities (H_I and H_{II}) of the sys-
tem in the two states (those in which it is before and after
the change, respectively).   This relation is derived by the
following consideration.   Suppose we start with the system
in the state I at the temperature T_1, and bring it into the
state II at the temperature T_2.   This result can be effected
in two ways, either by causing the change in state to take
place at T_1 and then changing the temperature of the system
to T_2, or by changing the temperature first to T_2 and then
causing the change in state to take place at that temperature.
The quantities of heat absorbed from the surroundings in the
two processes are,

$$Q_{T_1} + H_{II}\,(T_2 - T_1) \quad \text{and} \quad H_I\,(T_2 - T_1) + Q_{T_2},$$

respectively.   And since the initial and final states of the
system are the same, the initial and final values of its internal
energy must be the same, and therefore the quantities of heat
absorbed in the two processes of converting it from one of

these states to the other must be equal; for it has been assumed that no external work is done. Hence it follows that:

$$Q_{T_1} - Q_{T_2} = (H_I - H_{II})\,(T_2 - T_1).$$

It will be seen from this equation that the heat-effect attending the change of a system from one state to another is independent of the temperature when its heat-capacities in the two states are equal, and only in this case; and conversely.

As an example, consider the following application of the equation: The heat evolved by the combination of 2 grams of hydrogen with 16 grams of oxygen in a closed vessel at 20° is 67600 cal., and the specific heat-capacities (at constant volume) of hydrogen, oxygen, and liquid water are 2.41, 0.155, and 1.00, respectively. By substituting these values in the equation, the change of the heat-effect of the combination of the two gases with the temperature, and its value (Q_{T_2}) at any other temperature, such as 80°, are calculated as follows:

$$Q_{T_1} - Q_{T_2} = (2 \times 2.41 + 16 \times 0.155 - 18 \times 1.00)\,(80 - 20)$$
$$= -642 \text{ cal.}; \text{ whence follows, } -Q_{T_2} = 66958 \text{ cal.}$$

The above equation is of considerable importance from an experimental standpoint, since it is not practicable, owing to the errors from radiation, to make accurate calorimetric measurements of the heat-effect attending physical changes or chemical reactions at temperatures far removed from the room-temperature, and since, on the other hand, there is usually no difficulty in determining the heat-capacity of systems between the latter temperature and any higher or lower one.

In case quantities of work, W_{T_1} and W_{T_2}, are produced by the change in state at the two temperatures in addition to the quantities of heat absorbed (no work, however, being involved in the changes of the temperature of the system in either state), the equation expressing the identity of the change in internal energy in the two processes obviously becomes:

$$(Q_{T_1} - W_{T_1}) - (Q_{T_2} - W_{T_2}) = (H_I - H_{II})\,(T_2 - T_1).$$

If, in changing the temperature from T_1 to T_2, a change in state of aggregation takes place within the system, the heat-effect corresponding to this change, and also the heat-capacities of the system before and after it, must be taken into consideration in calculating the change in the heat of reaction with the temperature.   Although the special equation derived above is not applicable in this case, yet the same general principle consisting in equating the quantities of heat absorbed in two processes of transforming the system from a definite initial state at the one temperature to a definite final state at the other temperature is to be here employed.   Thus, in the example just considered, if the heat-effect of the combination of the hydrogen and oxygen to form water-*vapor* at 125° were to be calculated, it would be necessary to know the specific heat of vaporization of water at some temperature, say at 100°, and the specific heat-capacity of its vapor between that temperature and 125°.   Since the former value, when no external work is done, is 498 cals., and the latter value is 0.30, the heat of combination at 125° is — 57800 cal., as will be seen on making the calculation.

   35. **Chemical Energy.** — Chemical energy has been defined to be the energy that systems possess in virtue of the tendency of the substances composing them to undergo transformations into other substances.   The total decrease in the internal energy of a system in which a chemical change takes place is readily determined by measuring the heat-effect and work produced in the surroundings; but this cannot be placed equal to the decrease in chemical energy: for a chemical change is always accompanied, not only by a change in the chemical energy, that is, in the energy which gives rise to the tendency to the change, but also by changes in other forms of energy, namely, in the cohesion and disgregation energies of the system, or, otherwise expressed, in its heat energy, as is shown by the change in the system's heat-capacity which commonly accompanies the chemical change.   In certain special

cases, to be sure, the chemical energy can be separately determined; namely, where electrical energy is produced by the chemical change and the change can be made to take place in the reverse direction by imparting an equal amount of electrical energy to the system.

The resolution of chemical energy into factors has little significance from an experimental standpoint, since in most cases the numerical value of the energy itself is unknown; but it is sometimes convenient in theoretical discussions. The definitions of the factors that have been proposed do not, however, need to be presented here.

36. **Radiant Energy.** — Radiant energy has been defined to be the form in which energy is transmitted from one body to another without the mediation of matter, and it has been stated that there are different varieties of it called light, radiant heat, and electromagnetic radiations. These have, however, so many common characteristics that they are considered to be of essentially the same nature. For instance, it has been proved that the velocities with which light and electromagnetic radiations are transmitted through space are identical within the limits of the experimental errors, the value being 3.00×10^{10} centimeters, or 300 000 kilometers per second. Moreover, these three classes of radiations undergo reflection and refraction in accordance with the same laws, and they all exhibit the phenomena of interference and polarization.

The phenomenon of interference, that is, the fact that two rays when superposed under suitable conditions annihilate each other (two rays of light, for example, producing darkness), has led to the conclusion that radiant energy is transmitted in the form of *waves;* and, to facilitate the comprehension of the phenomena by making analogies possible with the wave phenomena exhibited by matter, it is conceived that the waves are propagated in a hypothetical medium, called the *ether,* and are the result of disturbances of some kind or other produced in it. The length of the

waves of radiant energy, or more briefly the *wave-length* (λ) of the rays, can be derived from the measurement of interference effects; and it is found in this way that its values are widely different in the cases of light or heat rays and of electromagnetic rays, and that there are smaller, though considerable differences in wave-length in the case of different rays of the same class, as in that of light rays of different colors. Thus, the smallest wave-length that has been measured, that of a ray thrown far beyond the violet end of the visible spectrum and detected by photographic means, is about 0.10 μ (μ representing one *micron* which is equal to 10^6 meters), the wave-lengths of the rays at the two limits of the visible spectrum are 0.36 and 0.81 μ, and the largest wave-length measured for any heat ray is 50 μ, while electromagnetic rays have been produced whose wave-lengths vary from 0.4 cm. to many kilometers. The similarity in kind of almost all the effects produced by these varieties of radiant energy has led to the conclusion that they differ *only* in wave-length, and therefore that the specification of this suffices to characterize them qualitatively.

The quantity of the effects produced by radiant energy is, however, determined by another characteristic of it, which is termed its *intensity* (ι), and which is defined, in general, as the quantity of radiant energy passing in a second through a square centimeter of area perpendicular to the rays. This may be determined in the case of light and heat rays by receiving them during a time r upon a blackened surface of area s perpendicular to the rays, by which they are absorbed and converted into heat, and measuring the quantity of heat Q produced; for by definition, $\iota = Q / sr$. For measuring the intensity of white light, as in photometry, a conventional system is usually employed, the illumination produced by the light upon a screen being made equal to that produced by some standard source of light by varying its distance from the screen; since *the intensity of light radiated uniformly in all direc-*

*tions varies inversely as the square of the distance of the re-
ceiving surface from the source,* the unknown intensity can
be readily calculated and expressed in terms of a conven-
tional unit.

The only phenomena connected with radiant energy
that require consideration here are those of the refraction,
polarization, absorption, and emission of light ; for these
alone have important relations to the chemical nature of
substances.

When a ray of light passes through a surface separat-
ing one medium from another, its direction is changed in
accordance with the following law, known as *Snell's Law of
Refraction: the incident and refracted rays and the normal
to the surface at the point of incidence are in the same plane,
and the sines of the angles which the two rays make with
that normal bear a constant ratio to each other.* That is, if
the incident and refracted rays make with the normal,
angles of θ_i and θ_r, respectively, $\sin \theta_i / \sin \theta_r = \nu$, where
ν is a quantity, called the *index of refraction,* constant with
reference to variations of θ_i and θ_r, but variable with the
character of the two media, especially with their densities
and chemical nature, and with the wave-length of the light.
When the incident ray passes from a vacuum into a second
medium, the corresponding value of ν is called the *absolute*
index of refraction of the medium. Ordinarily, however,
the index of refraction of a medium is determined and
stated with reference to the entrance of the ray into it
from air ; yet, since the absolute index for air under normal
conditions is 1.0003, the absolute index of a medium is only
0.03 per cent. greater than its index with reference to air,
and may usually be considered identical with it. It has
been proved experimentally, and has also been deduced
from the Wave Theory of Light, that the index of refrac-
tion of a medium is equal to the ratio of the velocity v_1
of light in air to its velocity v_2 in the medium ; that is,
$\nu = v_1 / v_2$.

When a ray of ordinary light passes perpendicularly through a plate of tourmaline properly cut with reference to the axes of the crystal, or is reflected from a mirror of transparent material (such as glass) at a suitable angle, it is found to have acquired the new characteristic of producing different effects upon its different sides ; for, when the same ray is passed perpendicularly through a second tourmaline plate, or is reflected from a second similar mirror, its final intensity is found to vary when the plate is rotated in a plane at right angles to the ray, or when the mirror is turned around the ray keeping the angle of incidence constant, and to have a minimum value of zero and a maximum value at two positions of the plate or mirror that are at right angles to each other. Light which produces such different effects in the various directions at right angles to the ray and a zero effect in one of those directions is said to be *plane-polarized*, or simply *polarized*. In order to facilitate the expression of these directions, it is agreed to select as a basis of reference the plane which embraces the incident ray and the normal to the mirror when it is in the position where the maximum amount of light is reflected, and to designate this the *plane of polarization.*

When a ray of polarized light passes through bodies of a certain crystalline structure, such as some varieties of quartz, or through bodies consisting of certain chemical substances, such as a tube of oil of turpentine or a solution of cane-sugar, its plane of polarization is rotated through a greater or less angle in the one direction or the other. This may be determined by examining the emerging ray with a glass mirror, a tourmaline, or other suitable analyzer. Substances which rotate the plane of polarization are called *optically active* substances : those that rotate it to the right when looking in the direction in which the light is traveling are called *right-rotating* or *dextro-rotatory* substances ; those which produce rotation in the opposite direction, *left-rotating* or *leavo-rotatory* substances. The angle of rotation ∝ is

found in the case of a homogeneous body to be exactly pro-
portional to the length l of the layer traversed by the ray,
and to increase, though not always proportionally, with the
density or concentration c of the active substance ; that is,
$\propto = \underset{\sim}{\propto} l c$, where $\underset{\sim}{\propto}$ is a quantity, called the *specific rotatory
power*, defined by this equation itself, constant with refer-
ence to variations of l, and usually, though not always,
approximately so with reference to those of c, and variable
in a high degree with the chemical substance and in a
smaller degree with the temperature and other physical
conditions, and with the wave-length of the light. In ex-
pressing numerical values of the specific rotatory power,
it is customary to employ the decimeter as the unit of
length and the gram per cubic centimeter as the unit
of concentration.

While only a very small proportion of known sub-
stances have in themselves the power of rotating the plane
of polarized light, all transparent substances acquire it in
variable degree when placed in a magnetic field, the effect
being strongest when the lines of force in the field are
parallel to the ray of light, and zero when they are per-
pendicular to it. For instance, when a ray of plane-polar-
ized light is passed through a tube of water around which
there is a helix of wire through which an electric current
is flowing, the plane of polarization of the emerging ray is
found to be different from that of the entering ray. This
phenomenon is known as *magnetic rotation* of the plane of
polarized light. The angle of rotation is proportional to the
strength of the current, or to that of the magnetic field
which it produces, and to the length of the layer submitted
to its influence and traversed by the ray. The direction of
the rotation is reversed when either that of the electric
current or that of the ray is reversed.

When a beam of light of any definite wave-length is
passed through a body, in general the intensity of the
emerging beam is found to be less than that of the enter-

ing beam, owing to the *absorption* of a portion of the light, and the conversion of it into heat, within the body. It is found that *a constant fraction of the light that enters each successive section of a homogeneous body is absorbed in that section, all the sections being considered to be of equal and indefinitely small thickness ;* or, expressed in mathematical form, if ι is the intensity of the beam at any distance l from the point of entrance, and $- d\iota$ is its decrease in intensity on traversing the further distance dl, then, $- d\iota / \iota = \beta \, dl$, where β is a quantity termed the *coefficient of absorption,* constant with reference to variations of ι and l, but variable with the nature and physical state of the substance and with the wave-length of the light. On integration, this equation gives, $\log (\iota_1 / \iota_2) = \beta \, l$, where ι_1 and ι_2 are the intensities of the entering and emerging beams, respectively, and l is the total length of the layer traversed.

It is found that the absorption-coefficient of gaseous substances at moderate pressure is very large for certain special wave-lengths, which vary with the nature of the gas, and practically zero for all other wave-lengths, so that if a beam of white light, such as is emitted by an incandescent solid, be passed through such gases and be resolved by a spectroscope, its spectrum is found to be crossed by a number of sharply defined dark lines corresponding to the wave-lengths for which practically complete absorption takes place. The values of these wave-lengths have been far more extensively determined and are of greater scientific importance than the values of the absorption-coefficients for definite wave-lengths. When the density of gases is increased by compression, the lines of their absorption-spectra become broader and less sharply defined at the edges. And in some liquids and solids the absorption takes place in such a manner as to produce in the spectrum one or more broad bands, each possessing a somewhat indefinite maximum of darkness and ill-defined limits. In other liquids the absorption-coefficient increases or

decreases continuously with increasing wave-length, or decreases to a minimum at some value of the wave-length and then increases continuously.

The phenomena of the absorption of light have additional interest, inasmuch as they are closely connected with the *color* of bodies, which is a property that arises usually from the unequal absorption out of white light of the rays of different wave-lengths, the impression produced on the eye being that caused by the unabsorbed rays. That selective absorption is the cause of the color of objects that are seen by transmitted light is obvious : but this is known to be, in most cases, also the source of the color of objects viewed by reflected light ; for the light, before it is reflected to the eye, generally traverses a layer of the substance of greater or less thickness. Thus, the colors of a piece of cobalt glass and of a potassium dichromate solution on the one hand, and of pigments on the other, are alike due to selective absorption. In some cases, to be sure, as in those of metals and solutions of many organic dyestuffs, the color is due to unequal reflection of the rays of different wave-lengths at the surface of the body, and is then termed *surface-color.* Bodies possessing surface-color must obviously show different colors according as they are viewed by reflected or transmitted light ; this is the case, for example, with gold, which is yellow by reflected light, and green, in very thin layers, by transmitted light, and with a strong solution of fuchsine, which is green by reflected, and red by transmitted light.

The *emission* of light by heated bodies is also closely connected with their powers of absorption and surface-reflection ; for, according to *Kirchhoff's Law, the rays of various wave-lengths are emitted by a heated body in the same proportion in which they are absorbed by it at the same temperature when they fall upon it from an external source.* In this statement, the proportion absorbed signifies the proportion of the incident ray that is neither reflected nor

transmitted.   For example, a heated mass of gas emits most copiously those rays that are absorbed most completely when white light from an external source is passed through it, and does not emit at all those rays that are transmitted through it without absorption; consequently, its emission-spectrum consists of bright lines corresponding exactly in position to the dark lines in its absorption-spectrum.   A piece of ruby glass, which appears red by transmitted light owing to absorption of the green rays, emits green light when heated to incandescence; and a mass of copper, which appears red owing to surface-reflection of the red rays, also emits green light when heated.

37.   **The Internal Energy of Gases.   Experiments of Gay-Lussac and of Joule and Thomson.** — In addition to the principles already discussed relating to the volume energy of gases and its factors, an extremely important law in regard to their internal energy has been discovered.   This may be stated as follows : *the internal energy of a definite quantity of any gas at a definite temperature is independent of its pressure or volume, provided the pressure is small.*

The validity of this law was first established by a series of experiments by Gay-Lussac, in which a gas, at a pressure of one atmosphere or half an atmosphere, contained in a large glass balloon was caused to expand suddenly, by opening a cock, into another balloon of the same volume in which a nearly perfect vacuum had been produced.   The temperatures within the two balloons, which were made equal before an experiment was performed, were carefully determined by means of delicate thermometers after the expansion had taken place. It was found that the rise of temperature which took place in the balloon originally empty was always equal, within the experimental error, to the fall of temperature occurring in the other balloon, so that, if the gas in the two balloons had been mixed, the original temperature would have been reproduced without any energy being imparted to or taken up from the surroundings, thus proving that the energy within a gas is

unaffected by a change of volume taking place at constant temperature.

Further experiments confirming the law were made by Joule, who substituted two copper cylinders for the glass balloons, immersed the whole apparatus in water, and determined the temperature of the latter before and after the expansion of air contained in one cylinder at 22 atmospheres' pressure into the other empty cylinder. No change of temperature could be detected.

This law, taken in connection with the Law of the Conservation of Energy, leads to two other important laws in regard to the energy-relations of gases under small pressures.

The first of these is as follows : *the heat absorbed from the surroundings by a gas kept at constant temperature while expanding against an external pressure is equivalent to the work done by it.* Since the energy of the gas itself remains unchanged, this law is an obvious consequence of the First Law of Energetics. That is, since the increase of energy of the system under consideration (the gas) is equal to zero, the equation expressing the First Law, $U_2 - U_1 = Q - W$, becomes $Q = W$. A gas under small pressure is therefore a system by means of which heat can be *quantitatively* transformed into work at constant temperature.

The second law deducible from the fundamental one first considered is that *the heat-capacity of a definite quantity of a gas is independent of its pressure or volume.* This follows at once from the principle stated in § 34 in regard to the relation between the heat-capacities of a system in two different states, and the heat-effects that accompany the change from one state to the other at different temperatures ; for, since the expansion of a gas when no external work is done is accompanied by the same heat-effect at any two different temperatures, namely, by *no* heat-effect at either temperature, the heat-capacities of the compressed and expanded gas are equal.

Later experiments of Joule and Thomson, made by a more exact method, show, however, that these laws are sub-

ject to deviations of the same order of magnitude as those
which affect Boyle's Law. In these experiments, which are
commonly known as the *porous-plug experiments*, the gas to
be investigated was driven by means of a force-pump, at a
perfectly uniform rate, first through a coil of pipes surrounded
with water, by which it was brought to a constant tempera-
ture, and then through a boxwood tube containing a porous
plug of unspun silk or cotton-wool and covered with insulating
material, which prevented any flow of heat to or from the
surroundings. After issuing from the plug, the gas was
allowed to escape into the atmosphere, or collected in a gas-
ometer at atmospheric pressure. The pressure of the gas
before it entered the plug was measured with a manometer;
this pressure could be varied in separate experiments by using
a more or less compact plug and by varying the quantity of
gas forced through it per second. After the gas had been
flowing so long that it was in thermal equilibrium with the
plug and surrounding tubes, its temperature was determined
by means of delicate thermometers just before it entered the
plug, and just after it issued from it. Since under these cir-
cumstances the gas in expanding absorbs no heat from the
surroundings, and does only an inconsiderable amount of work,
as will be seen below, the internal energy of the gas is
nearly the same after its expansion as it was before, and from
the observed difference in its temperature and its known heat-
capacity, the change in internal energy attending a corre-
sponding expansion of the gas at constant temperature can
be accurately deduced. Since the results are of fundamental
importance, the principles involved will be here presented.

Let the temperature, pressure, volume, and internal energy
of m grams of the gas just before it enters the porous plug
be t_1, p_1, v_1, and U_1, respectively, and the corresponding mag-
nitudes after the gas has issued from the plug in the expanded
condition be t_2, p_2, v_2', and U_2', respectively. Let the m
grams of gas then be heated at the constant pressure p_2 from
t_2 to t_1, whereby its volume becomes v_2, and its internal energy

U_2. It is desired now to determine the value $U_2 - U_1$, which represents the increase in the internal energy of m grams of the gas when at the constant temperature t_1 its volume increases from v_1 to v_2, or its pressure decreases from p_1 to p_2. In order to do this, we apply the general expression of the First Law, $U_2 - U_1 = Q - W$, successively to the two processes to which the gas has been subjected. In the first process, $Q = 0$; and $W = p_2v_2' - p_1v_1$, as will be evident from a reference to the accompanying figure, and from the consideration that when the gas enters the plug the volume v_1 is caused to disappear under the constant pressure p_1, and that when it issues from the plug the volume v_2' is produced
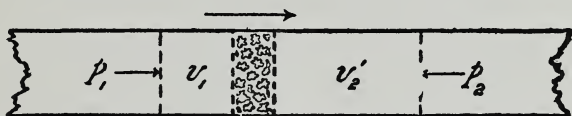
FIG. 5.

against the constant pressure p_2. It follows therefore that :

$$U_2' - U_1 = p_1v_1 - p_2v_2'.$$

In the second process, in which the gas is heated under the constant pressure p_2 from t_2 to t_1, it is evident that $Q = m\,H_p\,(t_1 - t_2)$, if H_p is the specific heat-capacity of the gas at constant pressure, and that $W = p_2\,(v_2 - v_2')$; therefore,

$$U_2 - U_2' = m\,H_p\,(t_1 - t_2) - p_2\,(v_2 - v_2'),$$

whence follows by combination with the foregoing equation,

$$U_2 - U_1 = m\,H_p\,(t_1 - t_2) + p_1v_1 - p_2v_2.$$

The evaluation of this change in internal energy obviously requires not only a knowledge of the temperature-change occurring in the porous-plug experiments, but also that of the heat-capacity of the gas at constant pressure and of the values of its pv-product at the two pressures in question ; both of these latter quantities have, however, been independently determined for most gases by direct measurements. It will be noted that the term $(p_1v_1 - p_2v_2)$ would

have the value zero for a gas that followed Boyle's Law, and that, according to the statements of § 21, since here p_1 is greater than p_2, it actually does have a small positive value for hydrogen and a small negative value for all other gases. The porous-plug experiments of Joule and Thomson show, however, that air, oxygen, nitrogen, and carbon dioxide undergo on expansion a *fall* of temperature, which corresponds to a positive value of $(t_1 - t_2)$, and that its magnitude is considerably more than sufficient to compensate the negative value of $(p_1v_1 - p_2v_2)$. Therefore, the internal energy of these gases increases when their volume increases and their temperature is kept constant. Incidentally, it is of interest to note the general magnitude of the fall of temperature observed; at 17°–20°, this was 0.26° with air, and 1.15° with carbon dioxide, for a decrease of pressure of one atmosphere. With hydrogen, on the other hand, a slight rise of temperature (0.033° for a pressure-decrease of one atmosphere) was observed in the porous-plug experiments; but its magnitude was not quite sufficient to compensate the positive value of $(p_1v_1 - p_2v_2)$, so that, apparently for this gas also, $(U_2 - U_1)$ has a positive value: it should be added, however, that in this case the calculated effect does not exceed the possible experimental error.

The best idea of the magnitude of this energy-increase can be obtained by comparing its value with that of the external work done when the gas expands against a pressure sensibly equal to its own. Computations have shown that, when the gas has a pressure of one atmosphere and undergoes an infinitesimal increase in volume, the ratio (dU / dW) of the increase in internal energy to the work done has at the room-temperature the value $\frac{1}{6000}$ in the case of hydrogen, $\frac{1}{420}$ in the case of air, and $\frac{1}{80}$ in the case of carbon dioxide; and that it has at 92° the value $\frac{1}{650}$ in the case of the last-named gas. The deviation from the fundamental law stating the constancy of the internal energy is therefore almost, if not quite, within the experimental error in the case

of hydrogen; very small, though undoubtedly real, in the case of air; much greater in the case of carbon dioxide; and, in its case, greater at the lower than the higher temperature. Thus, it is seen that the deviation is greater, the greater the deviation from Boyle's Law; and this justifies the inference that the former deviation would be zero in the case of a *perfect gas.* In the case of gases under high pressure, the law does not hold true even as an approximation; the cooling effect on expansion, even when no work is done, being then so great that it has been employed technically in the production of liquid air.

38. The Second Law of Energetics. — Besides the Law of its Conservation, another general principle relating to the transformation of energy has been empirically established. It has been found that, while other forms of energy are readily and completely transformed into heat, the transformation of heat into those other forms is subject to certain limitations. Thus, failure has attended all attempts to devise a machine or arrangement of matter which will do work in unlimited amount *merely* by withdrawing heat from the surroundings. An ideal process, in which heat is considered to be taken from surroundings of constant temperature and transformed into work by a system which itself undergoes no permanent modification, is called *perpetual motion of the second kind;* and a most extensive experience has shown that *perpetual motion of the second kind is impossible.* Experience with processes taking place at different temperatures has led to the conclusion that this principle is a consequence of a still more general natural law which may be expressed as follows: *a process whose final result is only a transformation of a quantity of heat into work is an impossibility.* This law is called the *Second Law of Energetics;* and this general statement of it will serve as a postulate forming the basis of the following considerations in regard to it.

As a concrete illustration of the Law, it may be men-

tioned that a process resulting solely in raising a weight and cooling a reservoir is an impossibility. Such a process would evidently not be a contradiction of the First Law; for this would only require that the work done and heat absorbed be equal. It may be further mentioned, by way of illustration, that, if the Second Law were not true, mechanical power could be obtained in unlimited quantities from the vast amount of heat present in the ocean, thus making unnecessary the fuel used in steamships as a source of energy.

The law, of course, does not imply that heat can not be transformed into work, but only that its transformation must be attended by a change in the condition of some other quantity of energy. This attendant change may be either a change in the condition of the energy of the surroundings, or in that of the system employed for the transformation; but it is always of such a character that the power of producing work which the surroundings or the system possesses is diminished.

The Second Law is based on an experience so extensive and varied that the probability of meeting with an exception to it is extremely slight; and especially so, in connection with mechanical or electrical processes. It is proved directly by the failure of all attempts to produce perpetual motion of the second kind, and indirectly by the quantitative correspondence of many conclusions drawn from it in regard to relations between different properties of substances, with those actually found to exist.

The Second Law is quite distinct in significance from the First Law, as may be made clearer by contrasting them. The First Law states that work can not be done by a system that undergoes no permanent modification, *except* by withdrawing energy of some form from the surroundings; in other words, that perpetual motion of the first kind is impossible. The Second Law states that work can not be done by such a system *merely* by withdrawing *heat* from the surroundings, that is, that perpetual motion of the second kind is impossible.

The First Law asserts that when a new quantity of energy appears in one form or at one place, an equivalent quantity of it of another form or at another place must disappear. The Second Law asserts that when a new quantity of work is produced by the transformation of heat, there must be an accompanying change in the condition of some other quantity of energy of such a character that the work it is capable of producing is correspondingly diminished.

39. Application of the Second Law to Changes Taking Place at a Constant Temperature. — The change attending the transformation of heat into work may be either a change in the condition of the transforming system or in that of the energy in the surroundings, as was stated above.

The first of these two cases is well illustrated by the expansion of a gas against an external pressure sensibly equal to its own; for a definite quantity of heat is thereby transformed into an equivalent amount of work, and the expanding gas, which is the system employed for the transformation, though it retains the same quantity of energy, so changes its condition (decreases its pressure and increases its volume) that its power of transforming heat is diminished.

The second case is that in which the system does not undergo any permanent change, but is in the same condition at the end of the processes to which it has been subjected as it was at the beginning. Such a series of processes is called a *cyclical process*. (It is to be noted that the term *process* is used both to express the way in which a change in the state of a system takes place, and also, as in this expression cyclical process, to designate a series of changes in state, each of which takes place in some definite manner.) If by such a process heat is to be transformed into work, the Second Law requires that an attendant change in the condition of the heat-energy in the surroundings take place. This change always consists in the passage of an additional quantity of heat from a state of higher, to one of lower temperature. Difference of temperature in the surroundings is therefore

an essential condition for the transformation of heat into work by a system which itself undergoes no permanent modification; otherwise expressed, *heat is not transformed into work by any cyclical process taking place in surroundings at a constant temperature.* This is merely a slightly different statement of the principle of the impossibility of perpetual motion of the second kind.

An illustration of a simple cyclical process taking place in surroundings at a constant temperature, and of the application to it of the principle just stated may be presented. Suppose that a gas is allowed to expand against an external pressure sensibly equal to or less than its own, and that it is then, by increasing the pressure, brought back to its original volume, it being kept in a large heat reservoir at constant temperature. The Second Law states that the work done by the gas in expanding, even under the most favorable conditions, can not be greater than that which must be expended upon it during the compression, since otherwise there would be a net gain of work in a cyclical process at constant temperature.

It is to be noted that the fact that difference of temperature is produced by the process itself does not invalidate the principle under consideration; for this requires that if a net gain of work is to result from a cyclical process, difference of temperature must exist in the *surroundings.* Thus, the fact that a gas in expanding rapidly against a pressure considerably less than its own falls in temperature, and thereby gives rise to a rapid flow of heat into it from the surroundings, does not increase the amount of work produced by the expansion, or make possible a net gain of work after the gas is restored to its original condition: on the contrary, as will be seen below, it has the opposite result — a net loss of work. When a change in a system takes place in such a manner that the system itself does not undergo an appreciable variation of temperature, the change and the process by which the change is effected are said to be *isothermal* ones.

The Second Law evidently permits that any change in a system which takes place of itself be capable of producing a definite *maximum quantity of external work*, namely, a quantity of work which is equal to, but not greater than, the quantity which must be expended in directly reversing the change, and thereby restoring the system to its original condition. And conversely, the Second Law requires that, in order to bring about a change in a system in the opposite direction to that in which it takes place of itself, only a definite *minimum quantity of external work* need be expended, namely, a quantity of work which is equal to, but not less than, the quantity which the reverse change is of itself capable of producing. It is, of course, possible, however, that the conditions under which the change takes place or is brought about, may be such as to produce *less* work than this maximum, or involve the expenditure of *more* work than this minimum quantity. And discrimination between processes of this kind and those that involve the maximum or minimum quantities of work is of fundamental importance in applications of the Second Law.

To distinguish these two kinds of processes, it is usual to employ the terms irreversible and reversible, which have, however, primarily, the following significance. A change in state, or the process by which it is effected, is called *reversible*, when the system can be directly restored to its original condition without giving rise to any residual effect in the surroundings. A change in state or a process is *irreversible* when this is not the case. For example, if a change in state is attended by the production of as much external work as would have to be expended in restoring the system to its original condition, it is obviously reversible; but if it produces less work than this, the change is evidently irreversible, for work would have to be withdrawn from the surroundings, in order to restore the system to its original state. Now, since the Second Law does not admit of the production of *more* work by a change than is required for its reversal,

it is evident that, when a change in a system is reversible, the maximum amount of work is produced which it is capable of producing, or the minimum amount of work is expended by which the change can be brought about; and that this is true *only* when it is reversible.

It is important to understand that the term reversible is always employed, in the manner just defined, to designate a change or process of such a character that it is possible to restore the original condition of things both in the system and its surroundings, not in the system alone. After an irreversible change has taken place, it is in general possible to restore the *system* to its original condition, but only by doing upon it a larger quantity of work than was obtained from it, so that the original condition in the *surroundings* is not reproduced. When an irreversible change has once taken place, it is not possible by any means whatever to reproduce in their entirety the conditions that previously existed.

Let us next consider the conditions that must be fulfilled, in order that an isothermal change may be reversible, or, what is equivalent to this, in order that it may produce the maximum amount of work. In the first place, it will be clear from a little consideration that *the change must take place under substantially the equilibrium-conditions*, the intensity of any form of energy that undergoes change within the system being compensated by a sensibly equal intensity externally applied; for, since the work produced by a change will be greater, the greater the magnitude of the latter intensity, this must be as great as is consistent with the occurrence of the change: the change will occur, however, if the external intensity is less than that within the system by only an infinitesimal amount. Similarly, since the work expended in producing the reverse change will be smaller, the smaller the value of the externally applied intensity, this must be as small as is consistent with the production of the change: the change can be brought about, however, by the external application of an intensity greater by only an infinitesimal amount than that corresponding to the equilibrium-condition.

Consider, as an example, a gas within a cylinder closed at the top by a piston on which a weight, producing any desired downward pressure, can be placed, the piston being held in position by a suitable stop by which it can be released when desired. It is evident, now, that the work that will be done if the gas expands will be greater, the greater the weight upon the piston ; but that the gas will not expand at all, if the weight on the piston gives rise to a greater downward pressure than the upward pressure of gas beneath. The maximum amount of work that can be obtained by the expansion will therefore be obtained when the externally applied pressure is sensibly equal to that of the gas. (Since that of the gas continually diminishes as its volume increases, the weight on the piston must of course be correspondingly decreased as the expansion progresses.) Similarly, the external pressure that must be applied in compressing the gas to its original volume, if the minimum amount of work is to be expended, must be greater than that of the gas by only an infinitesimal amount. It is further evident, since the pressure during the compression need be greater than that during the expansion by only an infinitesimal amount, that the amounts of work involved are sensibly equal when the two opposing changes take place under the equilibrium-conditions, and that therefore each of them is then reversible, since the gas can be restored to its original volume without producing any permanent change in the surroundings.

As another example, consider the conditions for the production of the maximum quantity of external work from a chemical change, such as that which takes place between a zinc plate and a copper sulphate solution. If the zinc is placed directly in the solution, the change is not attended by the production of any work whatever, and it is of course completely irreversible. If, however, the plate of zinc is placed in a zinc sulphate solution and a plate of copper is placed in a copper sulphate solution that is in contact with the zinc sulphate solution, it is found that a potential-

difference exists at the two plates, and that by suitably connecting them outside the cell, electrical energy, and secondarily other forms of energy, can be produced. If the plates are connected only by an ordinary metallic conductor, it is still true, however, that the only result is the production of a quantity of heat in the conductor owing to its electrical resistance, and the change is completely irreversible, just as in the former case, the only difference being that the heat is now produced in the surroundings instead of in the reacting mixture. But if the electromotive force of the cell be compensated by placing in the external circuit a storage cell or electric motor exerting an opposite electromotive force infinitesimally less than that of the cell, it is evident that the change then takes place under the equilibrium-conditions, and that it produces the maximum amount of work in the surroundings ; for, if the counter electromotive force were not less than that of the cell by an infinitesimal amount, the change would not take place at all, and, if it were less by a finite amount, a finite current would result, which would be attended by a finite Joule Heat-Effect and an equivalent decrease in the work produced. It is evident, moreover, that the change is then reversible ; for, if the external electromotive force be made greater than that of the cell by only an infinitesimal amount, electricity will flow in the opposite direction, the chemical change in the cell will take place in the reverse sense (zinc being precipitated and copper dissolved), and the quantity of electrical energy thereby expended in restoring the cell to its original state will be greater than that obtained from it by only an infinitesimal amount.

Another condition which must obviously be fulfilled, in order that a change may take place reversibly, is that the process which is essential to the production of the change, and which takes place under the equilibrium-conditions, be not attended by any other, irreversible process, that is, by any process by which work is converted into heat without producing such a change in the system or surroundings that the

work can be again obtained from the heat. Two such irreversible processes of extremely common occurrence are the production of heat by friction and by electrical resistance. Thus, in a reversible expansion or compression of a gas, the piston must move in the cylinder without friction; or, in a reversible transformation of the electrical energy produced by a voltaic battery into mechanical energy by means of an electric motor, the Joule Heat-Effect, and hence either the current-strength or the resistance of the circuit, must be zero.

From the characteristics of reversible changes just considered, it will be seen that no actually occurring changes are completely reversible; for, in order that a change may be such, it is necessary that there be only an infinitesimal difference of intensity within and without the system, and when this is the case, the time required for the occurrence of the change becomes infinite. Moreover, it is never possible to eliminate entirely such irreversible processes as the production of heat by friction or by electrical resistance. Reversible changes are therefore ideal changes representing a limiting condition which may be approached more or less closely in the case of actual changes, but is never attained by them. Since all actual changes are to a greater or less extent irreversible, the proportion of the existing energy that is transformable into work is continually diminishing.

The fact that reversible changes and processes constitute a limiting case, and one which involves the equilibrium-conditions of systems, makes the consideration of them of the greatest scientific value. It is therefore especially important to state explicitly the forms of the Second Law which are applicable to them. It is clear that the following principle in regard to them is a necessary consequence of the general statement of the Second Law and of the definition of reversible processes: *the algebraic sum of all the quantities of work produced in any isothermal reversible cyclical process is equal to zero;* for if the sum were greater than zero, the process itself, and if it were less than zero, the re-

versal of the process, would be a contradiction of the Second Law. This principle is essentially identical with the following one : *the quantity of external work produced when a definite change in the state of a system takes place at constant temperature is independent of the process by which the change is effected, provided only that it be a reversible one ;* for if two reversible processes of bringing about the same change in state produced different quantities of work, they could obviously be combined into a cyclical process yielding a quantity of work.

By the application of this principle many important conclusions in regard to the equilibrium-conditions of various systems and many relationships between the intensity-factors of different forms of energy within them have been derived. One of the common methods of deriving such conclusions and relationships is to consider an isothermal reversible cyclical process involving different forms of energy, or the same form under different conditions, to be carried out, to calculate the quantities of work involved in the different parts of the process, and to place their sum equal to zero, in accordance with the principle just stated.

This method may be illustrated by the following example, in which two different forms of energy are involved. Consider a system (a voltaic cell) composed of two platinum electrodes coated with platinum-black, each of which is half immersed in dilute sulphuric acid, the other half being exposed to hydrogen gas, which is contained at different pressures, p_1 and p_2, in two vessels of infinite capacity surrounding the upper parts of the two electrodes. An electromotive force is found to exist at the electrodes. Consider these to be connected with each other by a conducting medium of infinitesimal resistance, and that a counter electromotive force is introduced into the circuit. By this system an electric current, and therefore electrical energy, can be produced. The processes which attend this production of work are the absorption of hydrogen by the platinum electrode which is **in**

contact with the more compressed gas, the passage of this hydrogen from the electrode into solution, its precipitation on the other electrode, and its escape therefrom into the space containing the less compressed gas, the net change in the system therefore consisting in a transfer of some of the hydrogen from the vessel containing it at the higher to that containing it at the lower pressure. Moreover, it is found that the system can be restored to its original condition, that is, the process can be made to take place in the opposite direction and the hydrogen be brought back to the higher pressure, by making the counter electromotive force greater by an infinitesimal amount than that of the cell. It is therefore possible to carry out the process reversibly. In order now to determine how much electrical energy can be produced by a definite change in the system, and what the electromotive force of the cell is, we consider a process consisting of two parts to be carried out: 1. We transfer 1.0075 grams (one equivalent weight) of hydrogen from the vessel containing it at the higher pressure (p_1) to that containing it at the lower pressure (p_2) by means of the voltaic cell just described, the potential-difference of the cell being compensated by an opposite and sensibly equal potential-difference externally applied, for example, by placing in series with it a motor running at a suitable speed, so that the maximum amount of work will be obtained from it. 2. We compress the 1.0075 grams of hydrogen obtained in the vessel at lower pressure, with the help of a cylinder provided with a frictionless piston, until its pressure p_2 is brought back to its original value p_1. In order to do this reversibly, or with the expenditure of the minimum amount of work, we take care that the external pressure upon the piston be always greater than that of the gas beneath by only an infinitesimal amount. During both parts of the process we keep the system in a large heat reservoir of infinite extent, so that no difference of temperature is produced. An isothermal reversible cyclical process has now been carried out, and the Second Law requires that

the sum of the quantities of work, W_I and W_{II}, produced in the two parts of it, be equal to zero.   That is, since

$W_I = \varepsilon Q$ (by § 32), and $W_{II} = NRT \log(p_2 / p_1)$ (by § 30),

it follows that, $W_I + W_{II} = \varepsilon Q + NRT \log(p_2 / p_1) = 0$,

or that, $\quad\quad\quad \varepsilon Q = NRT \log(p_1 / p_2)$.

In this expression ε signifies the electromotive force of the cell, Q the quantity of electricity produced when one equivalent weight of hydrogen is transferred, N the number of mols of hydrogen transferred — in this case 0.5, since one mol of hydrogen is 2.015 grams or two equivalents, T the absolute temperature at which the change takes place, and R the gas-constant, which must be expressed in joules, if the electrical energy is to be so expressed, as is usually the case.   In order to determine the value of the electromotive force ε, additional knowledge is obviously required.   With the help of Faraday's Law and the electrochemical constant (§ 33) however, the calculation can be readily made ; for these require that, when one equivalent weight of hydrogen (or of any other substance) passes into solution or is precipitated in a voltaic cell, 96600 coulombs of electricity be under all circumstances developed. Thus, substituting the appropriate values in the above equation, we get, for a temperature of 20° :

$96600 \times \varepsilon = 0.5 \times 8.31 \times 293 \times 2.303 \log_{10}(p_1 / p_2)$ volts.

If the pressure in one vessel were two atmospheres, and that in the other, one atmosphere, $(p_1 / p_2) = 2$, $\varepsilon = 0.00874$ volts, and $W_I = \varepsilon Q = 843.8$ joules.

40. Application of the Second Law to Changes Taking Place at Different Temperatures. — It has been already seen that, when a quantity of heat is transformed into work by a system which undergoes no permanent modification, an additional quantity of heat is always taken up from surroundings at a higher temperature and is transferred to surroundings at a lower temperature.   That is to say, even when a difference of temperature exists, only a *fraction* of

the heat taken up by the system from the warmer surround-
ings can be transformed into work, if the system is to be
restored to its original condition. Important questions at
once arise as to what determines the fraction that can be
transformed: Is it dependent on the nature of the system
employed? And how does it vary with the temperatures?
To the consideration of these questions and to applications
of the conclusions reached this section will be devoted.

It should be first pointed out, however, if the maximum
amount of work is to be obtained by a process taking place
at different temperatures, that not only the two conditions
mentioned in § 39 must be fulfilled, namely, the occurrence of
all changes under the equilibrium-conditions and the absence
of any attendant essentially irreversible process, such as fric-
tion or electrical resistance ; but also that the changes in state
of the system must not be attended by the *direct* passage of
any quantity of heat from the surroundings at the higher,
to those at the lower temperature ; for example, no heat
must be transferred by processes of conduction or radiation.
For a quantity of heat so passing does not produce *any* work,
while under appropriate conditions a certain fraction of that
quantity of heat, as of any other quantity, can, of course, be
transformed into work. This third condition is, like the other
two, comprehended in the statement that a process produces
the maximum amount of work only when it is reversible.
For the direct flow of heat from a higher to a lower tem-
perature is essentially an irreversible process : the heat will
not, of itself, pass back to the body at the higher temper-
ature, and can not be brought there except by the expendi-
ture of work, that is, without producing a permanent change
in the surroundings.

In order now to determine whether the value of the
ratio of the quantity of heat that can be transformed into
work to the quantity transferred from the higher to the lower
temperature is dependent upon the nature of the system
employed for the transformation, or upon the way in which

the transformation is carried out, let us assume that two different reversible cyclical processes, carried out with different systems or in a different way with the same system, could produce two unequal quantities of work by transferring an equal quantity of heat from a higher to a lower temperature ; suppose now we cause the process that produces the larger amount of work (W'') to take place in such a way that it takes up a quantity of heat (Q_1) at the higher temperature (T_1), transfers a part of it (Q_2) to the lower temperature (T_2), and transforms the remainder into work (W''); and suppose we cause the other process, which in transferring the same quantity of heat (Q_2) from T_1 to T_2 produces the smaller amount of work (W'), to take place in the reverse direction — that is, so that it takes up the heat (Q_2) transferred by the former process to the lower temperature, and raises it to the higher temperature by expending the required amount of work (W').   It is then evident that the net result of these operations would be the production of a quantity of work ($W'' - W'$) from an equivalent quantity of heat without any other permanent change whatever having been brought about either in the systems or in the surroundings. Since this is contrary to the fundamental statement of the Second Law, the supposition made that the two processes produce unequal quantities of work is untenable.   That is to say, the quantity of work produced from a definite quantity of heat by any reversible cyclical process taking place at definite temperatures is independent of the system employed and of the way in which the process is carried out.   Or, since a reversible process produces the maximum amount of work, and since in a cyclical process the system is not permanently modified, this principle can be stated, without using these special terms, as follows : *The maximum amount of work which can be obtained when a definite quantity of heat is transferred from one temperature to another by any process in which the system employed undergoes no permanent modification is not dependent on the nature of the system or of the process.*

By the conclusion just reached the determination of the relation between temperature and the proportion of heat transformable into work is greatly facilitated; for evidently it is now only necessary to determine what that relation is for a single reversible cyclical process. We will therefore consider a process in which a definite quantity (N mols) of a perfect gas contained in a vessel closed with a weighted frictionless piston is employed as the transforming system, and we will assume that the temperatures involved are defined to be proportional to its pressures, instead of to those of hydrogen, as was done in § 22.

Suppose that the gas has in the beginning a volume v_1 and temperature T_1, and that the following process, consisting of four distinct parts, is carried out with it:

First, place it in a large heat-reservoir (for example, a large water-reservoir) at the temperature T_1, and, by gradually diminishing the weight on the piston, cause the gas to expand slowly until its volume becomes v_2. The gas does work during the expansion and tends to cool off, but is kept at constant temperature by an absorption of heat from the reservoir.

Second, make the piston immovable, so that the volume must remain constant, and withdraw heat from the gas until its temperature falls from T_1 to T_2; in order to do this reversibly, the gas is brought successively into communication with a series of heat-reservoirs varying continuously in temperature from T_1 to T_2, in such a manner that the gas always differs in temperature by only an infinitesimal amount from the reservoir with which it is in contact. The heat which the gas gives out in cooling, instead of all falling in temperature from T_1 to T_2, as would be the case if the gas were transferred directly to the heat-reservoir at T_2, is thus distributed among the reservoirs at the intermediate temperatures, and would evidently serve to heat the gas to its original temperature, whence it follows that the process is reversible.

Third, place the gas in a large heat-reservoir at the temperature T_2, and slowly compress it by releasing the piston and gradually increasing the weight upon it until the volume of the gas has been reduced from v_2 to its original volume v_1. Work is done on the gas during the compression, and it tends to become heated ; but it is kept at constant temperature by the reservoir with which it is surrounded, which absorbs the heat produced.

Fourth, again make the piston immovable, so as to keep the volume constant, and impart heat to the gas until its temperature rises from T_2 to T_1, making use of the series of reservoirs of continuously varying temperature employed in the second part of the process.

It is evident that the gas is now in its original condition, and that each of the changes which it has gone through has taken place in such a manner that it could be reversed without giving rise to any residual effect in the surroundings ; or, in other words, that a reversible cyclical process has been carried out.

Let us now proceed to determine the quantities of heat and work involved in the separate parts of this process, and from these, the net result of the process with respect to the transformation of heat into work.   In the first place, it is clear, since the volume of the gas was kept constant, that no work was done in the second and fourth parts of the process ; and furthermore, since the heat-capacity of a definite quantity of a perfect gas is independent of its pressure and volume (§ 37), that the heat given out by the gas to the reservoirs in the second part of the process is equal to that taken up by it from them in the fourth part.   Therefore, since no heat is transformed into work nor transferred from one temperature to another as a result of these two parts of the process, they can be entirely left out of consideration.

It remains only to consider the first and third parts of the process.   Designate the work produced in these two parts by W_1 and W_2, respectively, and the heat absorbed from the

surroundings in the two parts by Q_1 and Q_2, respectively. It follows then by § 30 that:

$$W_1 = N R\, T_1 \log \frac{v_2}{v_1}, \text{ and } W_2 = N R\, T_2 \log \frac{v_1}{v_2},$$

and therefore that the quantity of work produced by the whole process,

$$W = W_1 + W_2 = (T_1 - T_2)\, N R \log \frac{v_2}{v_1}.$$

It follows, furthermore, from the principle that the heat absorbed by a perfect gas in expanding at a constant temperature is equivalent to the work done by it (§ 37), that:

$$Q_1 = W_1 = T_1\, N R \log \frac{v_2}{v_1}.$$

Dividing the former of these two equations by the latter, we get an expression for the amount of work produced in the process above described, in terms of the quantity of heat absorbed from the surroundings at the higher temperature and the two temperatures involved; that is: $W = Q_1 \dfrac{T_1 - T_2}{T_1}.$

Since it has been shown above that the Second Law requires that the same quantity of work be produced from a definite quantity of heat by any reversible cyclical process whatever taking place at the same two temperatures, it is evident that this equation is an entirely general expression of the application of the Second Law to such processes. Thus, just the same final result is reached from the consideration of the quantities of work and heat involved in the separate parts of the process known as Carnot's Cyclical Process, in which a perfect gas undergoes a series of changes in pressure, volume, and temperature of a different character from those specified above: this process will be found described in treatises on Heat and Thermodynamics. Moreover, the ratio of work produced to heat absorbed would be the same if the system employed in the process were any other than a perfect gas; thus, this would be true in the case

of cyclical processes involving changes in the concentration and temperature of dilute solutions, which we now know how, at least in principle, to carry out reversibly.

The conclusion reached may be stated as follows : *The quantity of work produced in any reversible cyclical process in which a quantity of heat is absorbed by a system from surroundings at one temperature, and the portion of it not transformed into work is given off to surroundings at another temperature, is equal to the heat absorbed at the higher temperature multiplied by the difference of temperature and divided by the higher temperature expressed on the absolute scale. If the process is not reversible, a less amount of work is produced.*

Therefore, the maximum quantity of work (W) that can be obtained from a definite quantity of heat (Q_1) at any definite temperature (T_1) with the help of any system that undergoes no permanent modification is directly proportional to the difference between that temperature and any lower temperature (T_2) with which the system can be brought into communication. If the system can not be exposed to surroundings of different temperatures, no work can be produced by it, as was concluded in § 39 ; for, when $T_2 = T_1$, $W = 0$. If, on the other hand, it were practicable to bring the system into communication with surroundings at the absolute zero of temperature, it would possess the power of transforming the heat of surroundings at any higher temperature completely into work ; for, when $T_2 = 0$, $W = Q_1$. It will thus be seen that the general statement of the Second Law postulated at the start would not be true, if surroundings of great heat-capacity at the absolute zero of temperature were accessible to us ; but such surroundings are not accessible. It is further to be noted that the maximum amount of work obtainable from a definite quantity of heat, in different cases in which an equal difference of temperature exists in the surroundings, is inversely proportional to the higher temperature ; that is, if ($T_1 - T_2$) is constant, $W \propto (1 / T_1)$. Thus, a reversible cycli-

cal process taking place at 100° and 0° (on the normal tem-perature scale) would produce only $\frac{273}{373}$ as much work from a definite quantity of heat at 100° as one taking place at 0° and — 100° would produce from the same quantity of heat at 0°.

The temperatures T_1 and T_2 in the equation are those that would be measured by means of a thermometer contain-ing a constant volume of a perfect gas, instead of one of hydrogen as has been previously understood in accordance with the definition of § 22. But, since the experiments of Joule and Thomson show that in the case of hydrogen at temperatures between the freezing and boiling points of water the change in internal energy upon expansion is extremely small, the two temperature-scales are almost identical between those two temperatures. In fact, computations based on the data of the porous-plug experiments have shown, assuming the interval between the freezing and boiling points of water to be 100° on each scale, that the intermediate temperatures would not at any point differ by more than 0.003°, and that the calculated temperature of the freezing-point above the absolute zero would be within 0.1° of 273°, whether a hydro- . gen thermometer or a perfect-gas thermometer were employed for the measurements. It is not improbable, however, that the two scales differ to a considerable extent at very low temperatures.

It is also to be noted that a new definition of temper-ature — one that is not based on any property of any definite kind of substance, but merely on the characteristics of heat energy — can be founded upon the application of the Second Law to reversible cyclical processes of the kind just con-sidered. The result reached can be written in the form, $Q_1 / (- Q_2) = T_1 / T_2$, since by the First Law $W = Q_1 + Q_2$; and, in accordance with this equation, we may define the *ratio of any two temperatures* to be equal to the ratio of the heat absorbed at the one temperature to the heat evolved at the other temperature, when heat is transferred from the one to

the other by any reversible cyclical process whatever. The temperature-scale based upon this definition is called the *absolute energetic* (or *thermodynamic*) *temperature-scale.* It is absolute in the proper sense of the word; for, unlike the gas or mercury thermometer scales, its definition does not involve a relation to any property of any definite substance. Temperatures expressed on this scale are, of course, exactly identical with those that are proportional to the pressures that would be exhibited by a constant-volume thermometer filled with a perfect gas.

The principle derived above, which is expressed by the equation, $W = Q_1 (T_1 - T_2) / T_1$, is especially important by reason of the fact that it can be applied to determining the effect of temperature on the equilibrium-conditions of systems, or on the value of the intensity-factor of any form of energy that may be involved. An illustration of the way in which the principle is applied in obtaining such results may therefore be presented. Consider a reversible cyclical process carried out at two different temperatures with the hydrogen-gas-cell described in a previous example (§ 39). Let the process consist of the following parts : 1. Cause one equivalent of hydrogen to pass, with the help of the cell operating reversibly at the temperature T_1, from the vessel containing it at the higher pressure p_1, to that containing it at the lower pressure p_2. 2. Cool the gas so obtained by means of a series of heat reservoirs to a lower temperature T_2, keeping its volume constant, its pressure being thereby reduced to p_3. 3. By means of the voltaic cell, operating reversibly at the temperature T_2, transfer the hydrogen from a vessel in which the pressure is p_3 to one in which it has a higher value p_4, this last pressure being such that the gas will return to its original pressure p_1, if heated at constant volume to the temperature T_1. 4. Heat the gas so obtained by means of the series of heat reservoirs to the original temperature T_1, keeping its volume constant. The reversible cyclical process is then complete. As no work was done in the second and

fourth parts of the process, and as the heat given out by the gas in the second part was exactly compensated by that taken up by it in the fourth part, since the heat-capacity of a quantity of gas is independent of its pressure, these parts of the process can be entirely left out of consideration. Therefore, only the quantities of work and heat involved in the first and third parts need to be considered. If the electromotive force of the cell at T_1 is E_1 and at T_2 is E_2, and the quantity of electricity, which by Faraday's Law is the same in both cases, is Q, the work produced in the first part of the process is $E_1 Q$, and that expended in the third part is $E_2 Q$; the work W produced by the whole process is, therefore, $(E_1 - E_2) Q$. Substituting this value in the general equation, we get:

$$(E_1 - E_2) Q = Q_1 (T_1 - T_2) / T_1,$$

where Q_1 is the heat absorbed in the first part of the process. This equation evidently expresses a relation between the maximum quantities of electrical work which the cell is capable of producing at two different temperatures, or between the values of its electromotive force at two different temperatures, in terms of the heat-effect that attends the operation of the cell under the equilibrium-conditions at one of the two temperatures. This result is a typical one, being entirely analogous to those reached by other similar applications of the Second Law. In this special case, the work, $W_1 = E_1 Q$, produced in the first part of the process can be substituted for the heat Q_1 absorbed in it; for the two quantities are in this case equivalent, since a gas does not change its own energy-content when changed in pressure and volume at a constant temperature. Making this substitution, the last equation becomes simplified to the following one:

$$(E_1 - E_2) / E_1 = (T_1 - T_2) / T_1; \text{ or } E_1 / E_2 = T_1 / T_2;$$

which states that the fractional change in the electromotive force of the cell is equal to the fractional change in its absolute temperature, or that its electromotive force is proportional to its absolute temperature.

It is important to note that the above equation will yield exact results only when applied to reversible cyclical processes in which, as in those used for its derivation and illustration, quantities of heat are absorbed at one temperature and given out only at another temperature, and not at all at intermediate temperatures. In order that a process, consisting, like those described above, of a definite change in the state of a system at one temperature and the reverse change in its state at another temperature, may fulfil this last condition, it is evidently necessary that the heat-capacity of the system be the same in the two different states in which it exists during the cooling and during the heating. While this is almost exactly true for different volumes of the same quantity of any gas under moderate pressure, and for the different states of some other kinds of systems, it is not true in general. To cyclical processes carried out with systems for which it is not true, and consisting of changes of the kind just specified, the above equation is not rigidly applicable, though it will give, if applied to such processes, approximately correct results when the difference in the heat-capacities of the system in its two states is small, or when the temperature-difference involved is small.

It is evident, that, if the difference in the two temperatures be made infinitesimal, the heat-effects involved in the two parts of the process in which the system is cooled and heated, whether or not equal, will be infinitesimal, so that they can be neglected in comparison with the finite quantities of heat involved in the other two parts of the process. Therefore, if a reversible change of state takes place in any system whatever whereby a quantity of heat Q is absorbed from the surroundings at the temperature T, and a quantity of work W is produced in them, and the same change in state, but in the opposite direction, takes place at a slightly different temperature $T + dT$, and thereby a quantity of work equal to $-(W + dW)$ is produced in the surroundings, between these quantities of work and heat must obvi-

ously exist a relation entirely similar to that expressed by the equation, $W_1 + W_2 = Q_1 (T_1 - T_2) / T_1$, and one derivable from it by substitution; namely, since in this case, $W_1 = W$, $W_2 = -(W + dW)$, $Q_1 = Q$, $T_1 = T$, and $T_2 = T + dT$, it follows that:

$$dW = \frac{Q}{T} dT.$$

The quantity of heat Q involved in this equation is that which is absorbed by the system when the change in it takes place under reversible conditions. Since it is often not possible to measure this quantity of heat directly, it is convenient to substitute for it the quantity $W + (U_2 - U_1)$, which according to the First Law (§ 27) is equivalent to it. On making this substitution the above equation becomes:

$$W + (U_2 - U_1) = T \frac{dW}{dT}.$$

This equation is one of the most generally applicable expressions of the Second Law, and the exact significance of the symbols occurring in it should be fully appreciated. It is evident from the statements made in the foregoing deduction of the equation that W signifies the external work produced by any reversible change taking place in any system at a constant temperature $T;$ that $U_2 - U_1$ is the attendant increase in energy of the system itself, or the heat absorbed when the same change in it takes place without any external work being done; and that dW is the increase in the quantity of work produced when the same change in the system takes place at the temperature $T + dT$. And by the statement that the same change in the system is to take place at the two temperatures, it is to be understood that it changes from two such initial states as are converted into each other by the addition or withdrawal of heat alone, without any work being involved, to two such final states as are converted into each other in the same manner.

Since a change to be reversible must take place under the equilibrium-conditions, and since the quantity of work

produced by it is dependent upon those conditions, the above equation makes it possible to determine the effect of temperature on an equilibrium (by calculating dW / dT), when the other quantities (W and $U_2 - U_1$) involved in the equation are known. The quantity $U_2 - U_1$ can usually be readily determined by direct calorimetric measurements. In order to determine the quantity of work W, it is necessary to know the conditions under which the change in state will take place reversibly, that is, to know the value of the energy-intensity within the system (the surface-tension, pressure, elastic force, electromotive force, etc.) that must be compensated by an externally applied intensity in order to produce equilibrium, and thereby reversibility. The product of this intensity-value by the change in the value of the corresponding capacity-factor (the change in surface, volume, length, quantity of electricity, etc.) is equal to W, the maximum quantity of work that can be produced by the change in state under consideration. If the intensity-value varies during the change in state (as does the pressure of a gas upon expansion), the maximum work is given by a corresponding integral (for example, in the case of the gas, by $\int_{v_1}^{v_2} p \, dv$), and to evaluate this integral, it is necessary to know the law of the variation of the intensity during the change, that is, the functional relation between the intensity and capacity values (thus, between p and v in the case of the gas). All this knowledge must be derived, independently of the two Laws of Energetics, from established principles relating to the system in question, or through direct experimental investigations upon it.

The way in which the equation is applied in determining the effect of temperature on equilibrium-conditions may be illustrated by some examples.

Suppose it be desired to determine how the pressure of a quantity of hydrogen gas of constant volume changes with the temperature. Consider that the gas undergoes a change

of volume dv at each of two constant temperatures T and $T + dT$, the pressures of the gas in the two cases being p and $p + dp$, respectively. Then $U_2 - U_1 = 0$ by § 37; $W = p\,dv$; and $dW = dp\,dv$. Substituting in the general equation, we get:

$$p\,dv = T\frac{dp\,dv}{dT}, \text{ or } \frac{dp}{p} = \frac{dT}{T};$$

which states that the fractional change in the pressure of the gas when its volume is kept constant is equal to the fractional change in its absolute temperature, which is the basis of the determination of absolute temperature by the hydrogen thermometer.

As a second example, the hydrogen cell may be considered for which the relation between electromotive force and temperature was derived above by means of a cyclical process. The same relation can be deduced much more simply by substituting in the general equation the appropriate values; namely, putting $W = EQ$, $U_2 - U_1 = 0$, $dW = Q\,dE$, we get:

$$EQ = T\frac{Q\,dE}{dT}, \text{ or } \frac{dE}{E} = \frac{dT}{T}.$$

In order to determine the change in vapor-pressure of a pure liquid with the temperature, we consider that in a system consisting of the liquid and its vapor one mol of the liquid changes to vapor under the equilibrium-conditions at two different temperatures, T and $T + dT$. Let the vapor-pressure (that is, the pressure at which the liquid and vapor are in equilibrium) be p and $p + dp$ at the two temperatures, respectively, and let the volume of one mol of the liquid be V, and that of one mol of the vapor be v, when the pressure is p. Then $W = p(v - V)$; $W + U_2 - U_1 = ML$, the heat absorbed by the vaporization of one mol of liquid under the constant pressure p, which is the condition under which the calorimetric measurements are ordinarily made; and $dW = dp(v - V)$. Substituting these values we get:

$$ML = T(v - V)\frac{dp}{dT}.$$

This equation evidently gives a rigidly exact relation between the change of vapor-pressure of a substance with the temperature, its molar heat of vaporization, and its molar volumes in the state of liquid and saturated vapor. In this equation, if the vapor-pressure is small (for example, not much greater than one atmosphere) the volume of the liquid V can be neglected without great error in comparison with that of the vapor v, and for the latter, as an approximation, its value given by the gas-law-equation ($v = RT / p$, since $N = 1$) can be substituted. The above equation then becomes :

$$\frac{dp / p}{dT} = \frac{d \log p}{dT} = \frac{ML}{RT^2}.$$

The significance of this equation may be further illustrated, and its degree of accuracy demonstrated, by applying it to water at 100°. The specific heat of vaporization L of water at 100° is 537 calories, and its molecular weight is 18. Therefore $ML = 9670$ calories. Moreover, when expressed in calories, $R = 1.986$ (§ 30); and in this case, $T = 373$. Substituting these values in the foregoing equation, it is found that $(dp / p) / dT = 0.0350$. Actual measurements show that the vapor-pressure of water in centimeters of mercury is 73.32 at 99°, 76.00 at 100°, and 78.77 at 101°; so that the value of $(dp / p) / dT$, is 2.725 / 76.00, or 0.0359. The slight disagreement between this experimentally determined value and the calculated one is explained by the fact that water-vapor at 100° and atmospheric pressure is not a perfect gas and does not fully conform to the equation $pv = NRT$, as was assumed to be the case in simplifying the exact relation first obtained.

Since the fundamental equation, $dW / dT = Q / T = (W + U_2 - U_1) / T$, is a differential equation, it is, strictly speaking, only possible to deduce from it the effect of infinitesimal changes of temperature on the equilibrium of systems. The effect of finite changes can, however, be determined whenever this equation can be integrated between the desired temperature-limits. But, in order to do this, experimental data

must be available, which enable Q, the heat-effect attending the reversible change in state of the system, to be expressed as a function of the temperature between those limits.

Thus, in the example last considered, if it were desired to calculate the vapor-pressure of water at 30° from its value at 100°, it would be necessary to know the change of the heat of vaporization of water with the temperature. According to Regnault's determinations, this is expressed between those temperatures by the equation, $ML = 14330 - 12.51 \, T$. Dividing this value by that of R, substituting the result in the equation, $d \log p = ML \, dT / RT^2$, and integrating between the limits, $T = T_1, p = p_1$, and $T = T_2, p = p_2$, we get:

$$\log \frac{p_2}{p_1} = 7218 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) - 6.30 \log \frac{T_2}{T_1}.$$

Placing in this equation $p_2 = 76.00$, $T_2 = 373$, and $T_1 = 303$, noting that natural logarithms are to be employed, and solving, p_1 is found to be 3.23 cm. Actual measurements of the vapor-pressure at 30° show it to be 3.15 cm.

In concluding this discussion, attention may be called to the fact that the Second-Law equation can also be applied, in the opposite way, to the determination of the heat-effect that attends an isothermal reversible change in a system, when the effect of temperature on its equilibrium is known. Thus, the heat of vaporization of a liquid can evidently be calculated by the same equation as was used above in deriving the temperature-coefficient of its vapor-pressure, if the latter quantity has been experimentally determined.

APPENDIX I.

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APPENDIX II.

NOTATION.

In the system of notation used in this book each symbol represents, with a few unequivocal exceptions, only a single kind of physical quantity, and has in most of those cases in which usage is at all uniform, a significance in accordance with that usage. All physical quantities are represented by either Italic or Greek letters ; chemical substances and signs of operation (log, sin, etc.), by Roman letters. For all electrical and magnetic quantities, for time, and for quantities relating to chemical equivalents, small capitals are employed. For all optical quantities and for other quantities infrequently met with, small Greek letters are used. To represent specific properties, the same symbols are underlined ; thus v is volume in general, and $\underline{v}$ is specific volume. Different values of the same quantity are distinguished by numerical subscripts; a unique value by the subscript zero. The approximate values (always within 0.5 per cent.) of fundamental constants which it is well to remember, are printed in bold type ; for example, $g = \mathbf{980}$.

The following list shows the symbols employed and their significance.

a	Acceleration.	l	Length or Distance.
a, b	Van der Waals' constants.	m	Mass or Weight.
c	Energy capacity-factor. / Concentration in grams.	n	Molecule-coefficients.
		p	Pressure.
d	Differential.	q	Heat of reaction.
e	Base of natural logarithms.	r	Radius.
g	Acceleration due to gravity.	s	Surface or Cross-section.
h	Height.	t	Normal temperature.
i	Energy intensity-factor. / Van't Hoff's coefficient.	u	Velocity.
		v	Volume.
j	Gravitation-constant.	x	Fractional part (*e.g.*, content, dissociation, etc.)
k	Reaction-velocity-constant.		

A	Atomic weight.	M	Molecular weight.
C	Molar concentration.	N	Number of mols.
D	Density.	P	Osmotic pressure.
E	Energy.	Q	Heat-effect in general.
F	Force.	R	Gas-constant.
H	Heat-capacity.	S	Solubility.
J	Mechanical equivalent of heat.	T	Absolute temperature.
K	Equilibrium-constant.	U	Internal energy.
L	Heat-effect of vaporization or fusion.	V	Volume of non-gaseous phase.
		W	Work.

A	Equivalent weight.	N	Number of equivalents.
c	Equivalent concentration.	Q	Quantity of electricity.
E	Electromotive force.	R	Resistance.
I	Current-strength.	T	Time.
K	Dielectric-constant.	U	Velocity of ions.
L	Conductance.	V	Electrical potential.
M	Quantity of magnetism.		

α	Angle of rotation. / Empirical coefficient.	κ	Compression-coefficient. / Heat-capacity-ratio.
β	Absorption-coefficient. / Empirical coefficient.	λ	Wave-length of light.
		μ	Micron.
γ	Surface-tension.	ν	Index of refraction.
ε	Modulus of elasticity.	π	Ratio circumference to diameter.
θ	Angle.	ρ	Specific refraction.
ι	Intensity of light.	v	Velocity of light.

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